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MODELLING CORROSION & DEUTERIUM PICKUP IN ZR-2.5 WT% NB PRESSURE TUBES - STATUS REPORT

Report No 87-73-K

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ABSTRACT

Predictions of equivalent hydrogen levels in operating pressure tubes are required for reactor maintenance decisions such as SLAR, REFAB and RETUBE. There is little current data either from power reactor operation or laboratory exposures, that can be used to help predict the long-term in-reactor performance of Zr-2.5 wt% Nb in CANDU environments. At this time any predictions of pressure tube performance must be principally based on analysis of the limited data available from examination of CANDU removed pressure tubes. At present, there are two possible interpretations of this data; viz, the rate of deuterium uptake is accelerating with time, or a linear relationship exists between the rate of deuterium uptake and operating time for each pressure tube. These two interpretations lead to widely differing predictions and reactor maintenance decisions. This report is intended to review the analysis and interpretations of the data from removed pressure tubes. A draft version of this report has been reviewed by AECL-RC, OH-D&D, and OH-TTSD; reviewers' comments have been incorporated in this final report.

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82-107-40151	827.22	May 19, 1987	87-73-K

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EXECUTIVE SUMMARY

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B.D. Warr
Corrrosion & Tritium Technology Section
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Objective: To refine and update a computer model to predict corrosion and deuterium uptake in operating reactor pressure tubes. Predictions of equivalent hydrogen levels in operating reactor pressure tubes are required for reactor maintenance decisions such as SLAR, REFAB and RETUBE.

Key Results:

1. All available data on oxide thicknesses and deuterium concentrations from removed Zr-2.5 wt% Nb pressure tubes is presented, with interpretations of the data. Pressure tube data is extremely limited, and there is a lack of fundamental understanding of long-term corrosion and deuterium pickup processes in Zr-2.5 wt% Nb.

2. There are two main interpretations of the data. The first interpretation (which the author believes is slightly more probable), is that rates of deuterium pickup have accelerated in Pickering pressure tubes P4K10, P3F13 and P4N16. The second interpretation is that rates are linear, and differences between pressure tubes reflect scatter in the data probably as a result of differences in pressure tube material.

3. Equivalent hydrogen levels predicted for REFAB in Pickering 3 and 4 pressure tubes by 1995 and 2000 are 45 and 72 ppm respectively, assuming initial hydrogen levels of 10 ppm. These predictions are well above levels required for blister formation. For these predictions, rates of deuterium pickup are assumed to accelerate to a higher linear rate of 10.5 ppm/annum after 122 000 EFPH. Assuming linear rates of deuterium pickup with operating time, predictions of equivalent hydrogen are below that required for blister formation until at least 1995.

4. It is proposed that decomposition of the beta Zr phase occurring after long in-reactor exposures, may lead to rejection of Fe to form intermetallics which in turn results in accelerations in deuterium pickup rates. A threshold level of Fe (600 ppm for Pickering pressure tubes), may exist below which accelerated deuterium pickup does not occur.

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5. The role of Fe in pressure tube corrosion and deuterium pickup is uncertain. Based on the present data, it is not possible to substantiate a linear relationship between pressure tube Fe content and the rate of deuterium pickup in the pressure tube outlet region.

Recommendations:

1. Electron microscopical examinations of samples of removed Pickering pressure tubes are recommended to provide more information on changes in tube microstructures occurring in-reactor.

2. In order to 'break' the coincidentally increasing relationship between EFPH and pressure tube Fe content, it is recommended that the next pressure tube to be removed from Pickering 3 or 4 contain levels of Fe between 600-700 ppm.

3. The continued development of an accurate, reliable method for removing innocuous samples from pressure tubes for determination of oxide thickness and deuterium content in-situ is essential.

4. Analysis of pressure tubes removed from Pickering 8 should be performed to determine changes in composition and microstructure as a function of axial location.

5. Further data on deuterium concentrations should be obtained from Bruce pressure tubes X14 and N6 at the 580 cm location.

6. Ongoing experimental work will continue at OHRD and AECL-RC, and in conjunction with the Universities of Toronto, Windsor and McMaster, to develop an improved understanding of the long-term corrosion and deuterium pickup performance of Zr-2.5 wt% Nb including the effect of pressure tube material.

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MODELLING CORROSION AND DEUTERIUM PICKUP IN ZR-2.5 WT% NB PRESSURE TUBES - STATUS REPORT

1.0 Introduction

In a previous report/1/, predictions of oxide thicknesses and equivalent hydrogen (H) levels in Pickering 3 and 4 and Bruce 2 pressure tubes by 1990 were made. For these predictions linear or slightly increasing (quadratic) relationships were assumed between oxide thicknesses and deuterium concentrations with Effective Full Power Hours (EFPH).

Recently it has been necessary to predict equivalent H levels in Pickering 3 and 4 pressure tubes to 1995 and 2000/2/. These predictions are required for corporate decisions regarding SLAR and REFAB/RETUBE. Predicted levels of equivalent H at the location closest to the outlet where contact with the calandria tube is possible, in Pickering 3 and 4 pressure tubes, are 45 and 72 ppm by 1995 and 2000 respectively. These predictions are high since the rate of deuterium (D) ingress is assumed to accelerate along with an accelerating rate of oxidation, after a critical oxide thickness of 15 microns is reached. Similar assumptions have been made in predicting equivalent H levels in Darlington pressure tubes/3/.

As stated in the above references, there are many difficulties in analysing the data from different pressure tubes removed at different times in their operating histories. Since the above predictions were made, further data has been obtained from pressure tube P4K10, and included in the analysis. Also the basis for the predictions, and other possible interpretations of the data, have been discussed extensively with AECL-RC, OH-D&D, and OH-TTSD.

This report is intended to review the analysis of data from removed Zr-2.5 wt% Nb pressure tubes, and discuss the various interpretations. A draft version of this report has been reviewed by AECL-RC, OH-D&D, and OH-TTSD; reviewers' comments have been incorporated in this report. Preliminary results of experimental programs to evaluate the role of pressure tube material on the corrosion and D pickup rate will also be presented.

In the case of Zircaloy 2 pressure tubes removed from Pickering 1 and 2, oxidation rates were thought to accelerate rapidly once the oxide thickness measured on internal surfaces of pressure tubes reached approximately 15-20 microns. From the limited evidence available, B. Cox (AECL-RC) believes rates of deuterium pickup of up to 40 ppm D/ annum (20 ppm equivalent H) occurred once oxides reached approximately 30 microns.

Figure 1 shows a schematic of a possible relationship between oxide thickness and EFPH for Zr-2.5 wt% Nb, for two temperature regimes/1/. Shown in this figure is the onset of accelerating oxidation rate. The transition from a steady-state linear oxidation rate to a higher rate is usually referred to as 'breakaway'. In the case of Zircaloy 2 pressure tubes, the onset of breakaway oxidation was followed by increased rates of D uptake. Also, since oxidation rates increase with increasing temperature, breakaway will occur sooner at regions of the pressure tube close to the outlet. % D uptake (the proportion of D liberated by the corrosion process that is absorbed by the pressure tube) may also increase following the onset of breakaway. Thus, the relationship between D concentration and EFPH may show an increased slope, whilst following the same general trend as oxide thickness shown in Figure 1.

Although breakaway was observed in Zircaloy 2 pressure tubes, and has been observed in corrosion of other zirconium alloys, no conclusive evidence exists in the open literature/4,5,6/, as to whether it will occur in Zr-2.5 wt% Nb in the CANDU environment.

A long-term study of the oxidation of Zr-2.5 wt% Nb alloys in various environments was carried out for different material batches and thermomechanical treatments at AECL-RC/5/. Despite exposure durations of over 1000 days in water at 300°C, oxide thicknesses (estimated from weight gains) were too thin to have expected acceleration in oxidation rates. However, early post-transition behaviour of certain batches with its characteristic 'cyclic' behaviour was found to be similar to that of Zircaloy 2. Although this does not necessarily imply that subsequent acceleration of the oxidation rate should be expected, it does indicate similarities in the oxidation performance of both materials.

In a review of the worldwide literature on the degradation of zirconium alloys/4,6/, no conclusions could be reached regarding the potential for accelerated rates of D pickup in Zr-2.5 wt% Nb. However, there may be relevant data pertaining to this critical area from Russian-supported programs which has not been made available/7/.

Research programs at AECL and OHRD are expected to yield relevant data in the next several years. In the absence of any firm data to date, it has become necessary at this time to interpret data from lead pressure tubes as it becomes available. Since the data is extremely limited, any interpretations at this stage require a large degree of judgement. Due to the economics of pressure tube removal, there is unlikely to be sufficient data in the short term to allow for statistically meaningful analysis. However, given the importance of predicting D pickup rates as a function of time, and the lack of practically useful external data on Zr-2.5 wt% Nb, there is little practical option other than analysing and interpreting the data we have, whilst at the same time realizing its limitations.

Interpretation of data trends from several removed Zr-2.5 wt% Nb pressure tubes will always be difficult on account of the influences of individual fuel channel chemistries and material composition and thermomechanical processing. Thus, the continued development of an accurate, reliable method for periodically removing innocuous samples from the same pressure tube for determination of oxide thickness and deuterium content is essential. The long-term performance

of Zr-2.5 wt% Nb pressure tubes is unlikely to be resolved until several additional pressure tubes have been removed. Additional pressure tube removals are essential to improve our present data base and allow for improved decision-making. The correct choice of pressure tube for removal is important, and will be discussed later.

Further experimental work is ongoing at OHRD and AECL-RC, and in conjunction with the Universities of Toronto, Windsor and McMaster, to develop an improved understanding of the long-term corrosion and D pickup performance of Zr-2.5 wt% Nb including the effect of pressure tube material.

2.0 ANALYSIS OF DATA FROM REMOVED PRESSURE TUBES

For convenience, it is useful to treat the data in primarily two ways. In the first, all pressure tubes will be considered to be acting as a group. Secondly, their individual behaviour will be examined.

2.1 Pressure Tube Group Behaviour

2.1.1 D Concentration and Rate of D Uptake Versus EFPH

The preferred method of obtaining the relationship between rate of D uptake and EFPH is to obtain D concentrations after different EFPH along the lengths of the same group of selected pressure tubes in an operating reactor/8,9/. This is because the relationship may vary with pressure tube and differences in the environment in each tube/reactor unit. Using this approach, the time dependence of corrosion and D pickup for a given pressure tube can be followed.

In the absence of such data, it is necessary to assume similar behaviour for all removed pressure tubes, and examine the relationship between average D concentration and EFPH. By extending any fit of the data into the future, predictions may be made. Other possible reasons for any observed trends, such as differences in pressure tube material should also be examined.

In order to simplify data analysis, average uniform oxide thicknesses and D concentrations have been determined for each axial position for which data is available. Also, EFPHs have been chosen rather than 'Hot Hours', since it is found that the highest corrosion and D pickup occurs close to the pressure tube outlet. Presumably, this effect occurs during operation at or near full power, when the maximum estimated fuel channel temperatures are in effect.

In previous modelling/1/, data for all clock positions were shown. Generally there is a spread of this data at each axial position. In the case of Zircaloy 2 pressure tubes, oxide thicknesses were generally higher at the 6 o'clock position, presumably as a result of higher temperatures at this location. Associated D concentrations were generally found to be higher at the 12 o'clock location, presumably due to migration of D to the relatively colder location. For Zr-2.5 wt% Nb, considerably more scatter exists between oxide thicknesses and D concentrations for different clock positions at a given axial location. No trend was observed, as was found in the case of Zircaloy 2. Any scatter probably results from a combination of real differences occurring during operation and measurement error. In the case of D analysis, although exact determination of measurement error has not been made, it is estimated to be $\pm$10%. No attempt has been made to construct error bars from the data.

Figure 2a shows the range of D concentrations for all Zr-2.5 wt% Nb pressure tubes versus EFPH. Only data from the ends and middle of the pressure tubes are shown. Each point represents the average of all D concentrations taken at each axial position or ring. A number of observations may be made:

- Generally, the spread between minimum and maximum values of D concentration increase with EFPH.

- P3J9 data does not conform to the overall trend, with relatively low values of D concentration, and a small spread between maximum and minimum values.

- **Assuming group behaviour**, the average rate of D uptake at the outlet ends of pressure tubes (generally the maximum rate) is increasing with EFPH. A curve has been hand-drawn to illustrate this. Note that the absence of data from Bruce pressure tubes would not significantly affect the shape of this curve.

By fitting maximum D concentrations (at the 580 cm location), it is evident that the slope of the line is increasing with EFPH, with pronounced increases in slope after 80,000 EFPH.

In Figure 2b, the rate of D pickup is plotted versus EFPH. It appears from this figure that D pickup rates are increasing with time. This trend is particularly pronounced at the 580 cm, location as shown by the curve joining these points. (Note that J9 is not accounted for in this eyeball fit curve.) If it is assumed this is due to breakaway leading to accelerated rates of pickup, then it could be argued that in the case of K10, accelerated kinetics have been in effect for longer than N16 and F13. given its longer operating time. This argument will be discussed further in the analysis of individual behaviour of pressure tubes in Section 2.2.1.

One of the alternative interpretations referred to above is that for each pressure tube, rates of D pickup show a linear relationship with EFPH, with the individual behaviour of each pressure tube giving rise to the observed scatter. This is illustrated in Figure 2c, a plot of D concentration versus EFPH, taken from reference 9. The bands of D concentration shown for the 580 cm location for each pressure tube, represent the maximum and minimum measured for a given axial location. Since several bands contribute to the two pronounced peaks in the "probability of occurrence", the probability distribution is not necessarily valid. However, this figure serves to illustrate how predictions generated from the linear model will differ from those generated with the assumption of accelerated D pickup.

Predictions for Pickering 3 and 4 pressure tubes derived from accelerating or linear models are shown in Figure 3a, a plot of equivalent H versus EFPH. This is extended to show EFPH corresponding to 1995 and 2000 for Pickering 3 and 4. Note that initial H concentration is assumed to be 10 ppm.

Curve 1 in Figure 3a shows the relationship between equivalent H and EFPH assumed for the purpose of predictions/2/; ie, at 490 cm from the inlet, the most outboard location where contact with the calandria tube is predicted to be possible. One can see how the accelerated rate of D pickup parallels that found by extrapolation of the data for the 580 cm location (Curve 2). For curve 1, rates of D uptake are assumed to be initially in the order of 1 ppm/annum (7000 EFPH). Rates increase to over 10.5 ppm/annum, after 122 600 EFPH, the time taken to reach an oxide thickness of 15 microns at the 490 cm location. The selection of a critical oxide thickness at which accelerated D ingress occurs is convenient since we already have determined a temperature dependence of the oxidation rate/1/. Hence it is possible to calculate when the D uptake rate

will increase at various locations along the tube. There is no real basis for this assumption in Zr-2.5 wt% Nb, and the oxide thickness data appears to refute it (see Section 2.1.2). However, it does provide a time to accelerated ingress as a function of axial location which compares reasonably with that observed.

Note that it is possible to obtain higher rates of uptake (approximately 20 ppm D/7000 EFPH) than those shown in curve 2 in Figure 3a, by drawing the curve through the maximum D concentration at 580 cm for F13 and K10. Another important consideration is that if D pickup rates are accelerating, there may be further increases beyond our present data base. Thus it was felt that a D uptake rate of 10.5 ppm/annum is a reasonably conservative number (but not necessarily the worst case) to use for the predictions. Given the small data base, and other possible explanations for the above trend, it is premature to treat these predictions as anything other than extremely preliminary.

The line marked '3', extending through the equivalent hydrogen level for K10 at the 580 cm location compares predictions using the maximum linear rate observed from all Zr-2.5 wt% Nb pressure tubes removed to date.

Figure 3b shows comparisons of linear and accelerated predictions of equivalent H by 1995 versus distance from the inlet. Also shown are values of terminal solid solubility (TSS) and the equivalent H level above which blisters will form based on M. Leger's Scenario 3 (OHRD Report 86-153-k). Predictions with accelerated pickup remain below TSS over the entire pressure tube length, although well above the level for which blisters are predicted to occur between 350 and 490 cm. Assuming a linear rate of pickup, predicted equivalent H levels will not be sufficiently high for blisters to form in the contact region.

Predictions in Figure 3b are higher than those given previously in Figure 3a, since temperature profiles provided by D&D-NSD and taken from the Pickering B and Bruce B Design Manuals are used. These are higher than the estimated operating fuel channel temperatures provided by TTSD-CNS, and hence result in an earlier onset of accelerated D pickup.

2.1.2 Oxide Thickness Versus EFPH

Maximum uniform oxide thickness versus EFPH is shown in Figure 4a. As for the previous figures, each point represents the average of 4 clock position measurements taken in a ring from a given axial location. Again the wide range for each tube probably results mainly from the temperature dependence of the oxidation rate, oxides being thicker at the outlet compared to the inlet.

Rates of oxidation are plotted versus EFPH in Figure 4b. Initial oxide thicknesses are assumed to be 1 micron for all tubes. This figure clearly shows the relatively high rates of oxidation occurring in X14 and J11, and the lower rates for pressure tubes from Pickering 3 and 4, particularly K10.

There are some interesting observations here:

- K10 which had the highest rate of D pickup at the 580 cm location, also has the lowest oxidation rate. Oxidation rates and D pickup rates have been examined for all pressure tubes, and no obvious relationship has been observed between them. However, there is evidence that increased levels of Fe suppress oxidation rate and increase pickup rate (see Section 2.2.3.).

- Data from B2-X14 and J11 show higher rates of oxidation than other pressure tubes.

If acceleration in the D pickup rate has occurred, then the criteria developed for Zircaloy 2 requiring the formation of a critical oxide thickness (15-20 microns), does not appear to be valid for Zr-2.5 wt% Nb based on the above data. In the case of K10 this critical oxide thickness has not been reached, and yet it displays the highest D concentrations. Also, in J9 where oxide thicknesses have exceeded this critical value, D concentrations are very low.

Data on D concentrations is more reliable than that for oxide thicknesses, since the latter may be affected by spalling during operation, in-situ maintenance procedures such as 'SLARing', tube removal operations, and/or tube cutting and preparation for metallography. Maximum uniform oxide thicknesses reported are from areas where thick uniform oxides appear to be intact; ie, where no significant spalling is judged to have occurred. V. Urbanic (AECL-RC), believes that should oxide spalling have occurred prior to measurement it is unlikely to affect this measurement significantly. Assuming spalling has only occurred in K10, then oxide thicknesses of about 23 microns (or about twice that measured), would be required for the data to conform to the general trend. If significant spalling has occurred on K10, it appears to be the only pressure tube displaying such behaviour.

If K10 oxide thickness data is real, and acceleration in D pickup rates have occurred, we should examine criteria other than 'critical oxide thickness'. One such possibility is that pressure tube material transformations occurring in-reactor lead to accelerated D pickup - this will be examined in later sections.

In order to examine these areas further, it is necessary to review in more detail the individual behaviour of each of the removed pressure tubes.

2.2 Pressure Tube Individual Behaviour

2.2.1 Oxidation Rate and D Pickup Rate Versus Distance/Temperature

Figure 5 shows pressure tube oxidation rate versus distance for the four Pickering pressure tubes. In this and successive figures, lines have been placed between points to ease interpretation. However, they are not intended to infer the shape of the relationship between the data points, and may be misleading. Key observations are as follows:

- K10 shows the lowest oxidation rates.

- With the possible exception of J9, slightly positive or negative increases in oxidation rate are observed up to 300 cm. from the pressure tube inlet. Following this point, rates of oxidation increase with distance. In the previous modelling report, it was concluded that this effect was primarily caused by the temperature dependence of the oxidation rate. There may also be a possible inverse effect of neutron irradiation which suppresses the oxidation rate in the centre of the pressure tube, and possibly more oxidizing conditions as we approach the outlet.

- J9 is the only pressure tube showing an apparent continuous increase in oxidation rate with distance.

With reference to Figure 6a which shows D pickup rate versus distance from the inlet for Pickering pressure tubes:

- In both F13 and K10, the longest running tubes with approximately the same EFPH (91 100 and 92 500 respectively), rates of increase of D pickup rate towards the outlet end are highest and may extend further inboard than N16 and J9. Further D measurements are required on F13 at the 400-500 cm region to determine the extent to which acceleration has progressed inboard. This may imply that rates of D pickup have increased first at the outlet region, and moved closer to the inlet, giving the apparent higher slope (probably mainly as a result of temperature dependence). In N16 this effect is less pronounced, and in J9 may not yet have occurred at all.

- There is considerable variation in D pickup rates between pressure tubes, with the spread increasing from inlet to outlet regions.

- The ranking of each pressure tube (with the exception of J9 which remains the lowest) changes with distance. It has been proposed/10,11/ that differences in pressure tube material account for observed differences in rates of D pickup. However, any explanation based on this should be able to accommodate the change of ranking with distance. It is possible, though unlikely, that axial variations in impurity content and pressure tube material could account for these changes in ranking. V. Urbanic (AECL-RC) has pointed out that local chemistry variations may also play a role.

- J9 displays unusual behaviour in which the rate of D pickup remains virtually flat along the entire pressure tube. This could be interpreted to imply that D pickup rates have not (yet) accelerated in J9.

- K10 shows the highest and most uniform slope (apparent temperature dependence) of the rate of D pickup rate.

- F13 and N16 show D pickup rate to be decreasing with temperature up to about 340 cm, followed by increases in D pickup. V. Urbanic (AECL-RC) has pointed out that a similar decrease in D concentration was observed in Zircaloy 2 pressure tubes up to the 200 cm. location, before increases were seen. This was explained on the basis of increasing oxidizing conditions along the pressure tubes due to radiolysis, in a water chemistry which was 'borderline' in terms of control of dissolved H_2.

For comparison, D pickup rates of Bruce 2 pressure tubes versus distance are shown in Figure 6b:

- D pickup rates are similar to those for Pickering pressure tubes.

- Pressure tubes maintain their ranking with distance.

- Generally, there appears to be a continuous increase of D pickup rate with distance. B. Cox (AECL-RC) notes that higher average D levels were present in the coolant in Bruce 2 compared to Pickering 3 and 4. This may have led to less variation in water chemistry along the channels. Also, differences in channel flow and fluences caused by fuelling variations might have contributed to these observations.

- Further data is required from X14 and N6 at the 590 cm location. With the present data, based on the above arguments for Pickering pressure tubes, it appears that acceleration in D pickup rate has not yet occurred.

The relationship between distance from the inlet and temperature for operating pressure tubes is uncertain due to the difficulty in collecting accurate data. Hence it is preferred to show relationships versus distance which is known. In Figure 6c, D pickup rates are plotted versus temperature for Pickering pressure tubes. The relationship between temperature and distance provided by D&D-NSD and contained in the Pickering B and Bruce B Design Manuals has been taken. The plots are quite similar to those shown in Figure 6a, although the effect of the increased D pickup rate at the 580 cm location (corresponding to a temperature of 296°C) is greater. This is because the temperature profile is quite flat in this region.

2.2.2 % Theoretical D Pickup Versus Distance

Figure 7 shows the % theoretical D pickup versus distance from the inlet for Pickering 3 and 4 pressure tubes. Key observations are:

- K10 is the only pressure tube showing a significant and uniform apparent temperature dependence of % theoretical D pickup.
- J9 has a decreasing % pickup with distance.
- N16 and F13 show a virtually flat relationship.

A similar plot for Bruce pressure tubes is not included due to lack of data.

2.2.3 Effects of Pressure Tube Material

2.2.3.1 Effect on D Pickup

It has been proposed that pressure tube impurity content, particularly Fe, and possibly other elements such as Cr, Ni, and C may explain differences in the rate of D pickup. R. Ploc (AECL-RC) has noted that relationships between impurity content and rates of D pickup should account for solubilities of the impurity elements/12/.

Several sources of analyses are now available. For pressure tubes referred to in this report (excepting K10 and N6 where offcuts were not available), AECL-RC have had samples from offcuts analysed at Western Zirconium/13/. Reported values for most elements, are given as 'less than, not allowing for meaningful comparison with ingot analyses.

Comparisons of analyses of other pressure tubes are also available. At OHRD samples of pressure tubes, offcuts and hardness rings, with varying impurity levels are being exposed in static autoclaves (D_2O, pH 10.5, 340 and 350°C) in order to examine relationships between rates of oxidation and D pickup, and pressure tube material factors such as impurity content and grain size.

Analysis of 14 of these samples have also been performed at Western Zirconium and Teledyne Wah Chang. Ten of these samples were taken from pressure tubes removed from Pickering 8 and four were taken from offcuts from Bruce A pressure tubes. Results of these analyses are compared with ingot analyses in Appendix 1. In the bar charts shown in alphabetical order by element in Appendix 1, the original ingot analysis from the location corresponding to the pressure tube, is shown as Ingot(WC). The two more recent analyses are shown as PT(WZ) and PT(WC) - analyses performed at Western Zirconium and Teledyne Wah Chang (two samples only),

respectively. Many figures in Appendix I show values of 'less than' generally 10 ppm. Thus these elements were not considered further in developing correlations. As expected, H concentrations found in offcuts/pressure tubes are generally higher than those found in ingots. This is probably due to H pickup primarily during the pickling, and possibly extrusion, processes. Hf concentrations are shown to be quite similar for all samples at 40-50 ppm. Ni levels are generally low, at <20 ppm.

Thus, for pressure tubes, relationships between the rate of D uptake (and oxidation rates) and levels of Fe, Cr, C, O, N, Si, Al and Nb have been examined; ie, all the elements for which there is reasonable data with significant concentrations and measurable differences between samples. Levels of the other impurities are generally low and show a sufficiently small variation between pressure tubes in the present population, that their effect is unlikely to be substantial. However, further work may be required to confirm this.

Only for Fe and Cr and to a lesser extent Si, have possible correlations between maximum rates of pickup and impurity level been observed. For these three elements, there is an apparent increasing relationship between D pickup rates at the outlet region (580 cm), and impurity concentration as has been previously observed for Fe and Cr/13/. For data taken from the tube midpoint (290-350 cm), and closer to the inlet (50-80 cm), no trend was observed. Note that average values of D pickup for each pressure tube are not included since these will be biased by the number and location of sampling points.

In Figure 8a, D pickup rates at the three locations are plotted versus Fe concentration for all pressure tubes. Fe concentrations were taken from offcut analyses except in the case of K10 and N6 where they were not available and average ingot analyses were used. With reference to Figure 8a:

- For the maximum rate of D uptake, at an axial location of approximately 580 cm from the inlet, there is an apparent increasing relationship with Fe content.

- J9 displays relatively low rates of D pickup.

- For D uptake rates taken at the tube mid-point (290-350 cm) and inlet regions (50-80 cm) there is insufficient spread in the data to determine if a similar trend is occurring.

As a result of the small spread of D pickup rates at the tube mid-points and inlet regions, only data at the 580 cm location will be examined further. With respect to Figure 8b:

- If the trends for Bruce and Pickering pressure tubes are examined separately, they appear to display differing relationships as shown. No data is available for X14 and N6 at the 580 cm location.

- Despite the large difference in Fe content between F13 (offcut analysis) and K10 (ingot analysis), their respective D uptake rates are quite similar.

- Differences in pickup rates are most pronounced between J9, N16 and F13, despite the relatively small difference in Fe contents (~200 ppm) between these tubes.

- Insufficient data is available from Bruce 2 pressure tubes to develop a relationship.

Also the relationship depends on the source taken for Fe analysis. Figure 8c shows a similar plot for Pickering pressure tubes using the average Fe content taken from the ingot analyses. Here, the large difference in pickup rate between J9 and F13 occurs with a difference in Fe concentration of <100 ppm. Also N16 has a higher Fe content but lower pickup rate than F13. For the above reasons it is not possible at this stage to derive a simple linear relationship between Fe content and D pickup rate in outlet regions of Zr-2.5 wt% Nb pressure tubes.

Discussions with staff at AECL-RC would indicate that we would not necessarily expect a linear relationship, but rather the relationship shown in Figure 8b (dotted line) for the Pickering tubes, if the effect of Fe is correlated with the presence of Zr_2Fe precipitates which may act as preferential routes for the absorbtion of D. Assuming these precipitates are only present once a threshold level of Fe is reached, say between 400-600 ppm, then it would be expected that D pickup rates would begin to increase sharply beyond that level as observed in data from the Pickering pressure tubes. Also, the D pickup rate may saturate once a critical level of intermetallics have been formed. This would explain the relatively small difference in D pickup between pressure tubes F13 and K10. Differences between Pickering and Bruce pressure tubes may arise as a result of their minor differences in structure, leading to variation in the partitioning of Fe in the beta-Zr phase, and possibly higher effective solubilities in the case of the Pickering pressure tubes. This argument will be further developed in Section 3 to incorporate the effects of decomposition of the beta Zr phase during in-reactor exposures.

Fe is known to form intermetallics which can promote D absorbtion. Samples of pressure tubes from Pickering 8 and Bruce 2, with levels of Fe ranging from 300-700 ppm, have been examined at the University of Windsor by transmission electron microscopy. Intermetallic particles have been observed in samples with Fe contents above 490 ppm. These intermetallics were identified as Zr_2Fe. These results would tend to support the concept of a threshold level of Fe being required before increases in D pickup are observed. Detailed results of this work are given in Appendix 2. The ramifications of a threshold Fe level relative to specification of new pressure tubes or identifying pressure tubes with highest rates of D pickup are quite different from those obtained provided the linear relationship is valid. Since the threshold level of Fe will depend on pressure tube thermomechanical treatment, specifications designed to minimize D pickup may vary with such treatment.

Figures 9a and 9b show the relationship between D pickup rate at 580 cm and Cr and Si contents, taken from offcut/ingot analyses, respectively. For Pickering tubes, the relationship appears to be similar to that found in the case of Fe. For Cr, D pickup rate appears to increase with increasing levels of the impurity element. As with the relationship with Fe, the spread in data from Bruce pressure tubes is too small to allow for meaningful interpretation. In Figure 9b, K10 with the highest D pickup rate also has the highest Si content. The remaining pressure tubes containing between 30-50 ppm Si show a large variation in pickup rate.

2.2.3.2 Effect on Oxidation Rate

Relationships between oxidation rate and impurity content have also been examined, and in no cases were obvious trends observed. In Figure 10, oxidation rate is plotted versus Fe content. As observed in previous figures, K10 with highest levels of Fe shows relatively low values of apparent oxidation rate.

Samples from beta and non beta-quenched offcuts with Fe contents ranging from 300-1500 ppm have been exposed in static autoclaves for 30 days in D_2O, pH 10.5, at 350°C. Preliminary

results of this OHRD experimental program show oxidation rate to be decreasing with increasing levels of Fe, over the range 300-1500 ppm. Beta-quenched samples showed lower oxidation rates than non beta-quenched samples. Work is ongoing to confirm these results with a larger number of samples, longer exposure times and various temperatures. This program should provide further data to improve our knowledge and understanding of relationships between impurity content and rates of oxidation of D pickup.

3.0 DISCUSSION

3.1 Interpretations of the Data and Predictions

All available data on oxide thicknesses and D concentrations has been presented above with various possible interpretations. The major question for which there is presently insufficient evidence to reach a definitive conclusion, remains the relationship between the rate of D pickup and operating time after long in-reactor exposures (greater than approximately 90,000 EFPH). Presently, there are two main interpretations of the data, each resulting in widely differing rates of D pickup and predictions. Viz, (i) rates of D pickup have accelerated in Pickering pressure tubes K10, F13 and N16, or (ii) there is a linear relationship between D pickup rate and time for each pressure tube, with the observed scatter between tubes being due to material differences.

These two interpretations result in quite different predictions for equivalent H in pressure tubes, and impact greatly on reactor maintenance decisions such as REFAB or RETUBE. For predictions based on an acceleration in D pickup rate, the rate increase was assumed to occur once the oxide thickness reached 15 microns. There is currently insufficient basis for this assumption. However it does result in similar predicted times to accelerated D pickup as those observed, and it provides a relationship between distance from the inlet (or temperature) and time taken for a rate increase to occur. Based on D pickup rates accelerating to 10.5 ppm/annum after 15 microns (122 000 EFPH), (model 1 in Figure 3a), equivalent H levels of 45 ppm have been predicted for the 490 cm location of Pickering 3 and 4 pressure tubes by 1995. With the worst-case linear model, equivalent H levels should not exceed 25 ppm for the same location. An initial H level of 10 ppm is assumed for predictions. Predictions with accelerated pickup remain below terminal solid solubility over the entire pressure tube length, although well above the level for which blisters are predicted to occur between 350 and 490 cm. Assuming a maximum linear rate of pickup, predicted equivalent H levels will not be sufficiently high for blisters to form in the contact region.

Despite the paucity and inconclusive nature of the data available, this author's judgment is that it is slightly more probable that D pickup rates are already tending to accelerate. This acceleration has probably occurred in the three Pickering pressure tubes (P4K10, P3F13 and P4N16), which show significantly higher D pickup rates in the outlet region compared to the body of the tubes. These rate increases will occur first at higher temperatures, and then gradually move down the pressure tube towards the inlet with increasing EFPH (see Figure 1). This acceleration may have extended further inboard, in pressure tubes with the highest EFPH, the effect being most pronounced on K10. Both the group and individual behaviour of Pickering pressure tubes can be explained on the basis of an acceleration in D pickup rate. In pressure tube J9 where no such increase in D pickup rate was observed, an acceleration in rate may not yet have occurred.

3.2 Possible Reasons for Acceleration in D Pickup Rates

D pickup rates in the four Pickering pressure tubes increase with increasing Fe content at approximately 580 cm from the inlet. Based on the limited data a linear relationship does not appear to exist between D pickup rate at the 580 cm location, and Fe content. It is more

probable that there is a threshold level of Fe, which in turn may be a function of pressure tube thermomechanical history. For Pickering pressure tubes the threshold appears to be approximately 600 ppm Fe. Bruce tubes may have a different, possibly lower threshold.

Assuming the accelerating argument is valid, there remains the question of why it is taking place. With reference to Figure 3, acceleration in D pickup rate at the 580 cm location appears to have occurred after approximately 80,000 EFPH. In Zircaloy 2, an argument was developed that acceleration in first the oxidation rate, followed by D pickup rates, occurred after a critical oxide thickness of 15-20 microns was reached. But a trend towards increasing D pickup rate with oxidation rate has not yet been observed in the above data for Zr-2.5 wt% Nb. In fact, K10 with the highest D pickup rate at the 580 cm location appears to have the lowest oxidation rate of all four Pickering pressure tubes. J9 displays no increase in D pickup rate along its length, although it shows the most consistent increase in oxidation rate.

Also, while there is a trend towards increasing D pickup rate at the 580 cm location with Fe content, no such relationship is evident with respect to oxidation rate. This may be attributed to the unreliable nature of oxide thickness measurements due to possible spalling or oxide removal prior to measurement. It may also be pointing to a criterion other than a critical oxide thickness, for significant observable acceleration in D pickup rates to occur. The most obvious area we should consider here is changes that may be occurring in the pressure tube material with operating time.

Electron microscopical examination was performed on B2 X14 following pressure tube removal after 31 200 EFPH/14/. Some decomposition of the beta Zr phase into beta Nb and omega phase precipitates was observed. Although no further pressure tubes have been similarly examined after longer exposure times, it is reasonable to assume that this process of decomposition of the beta phase will increase with in-reactor exposure. Although precise values of solubilities are probably not available, Fe solubility in the beta Zr phase is known to be higher than that in the alpha Zr or beta Nb phases. Thus, during the decomposition of beta Zr to beta Nb, Fe will be rejected, probably to form small intermetallics of Zr_2Fe. Assuming the temperature is the major driving force for decomposition, the greatest amount of decomposition of the beta Zr will occur in the high temperature regions close to the pressure tube outlet. Lesser amounts of decomposition will occur as the inlet is approached. In tubes with higher Fe contents (assuming the beta Zr phase is not saturated with Fe), for a given amount of beta Zr decomposition to beta Nb, more Fe is made available for the formation of intermetallics.

No literature is available on the effect of Fe contents in the range found in Zr-2.5 wt% Nb pressure tubes. Results of ASTM accelerated G2 corrosion tests available in pressure tube history dockets have been analysed/15/. No significant correlation was observed between weight gain and Fe contents of samples tested. For Zircaloy 2, where larger numbers of intermetallics are present, there may be an increasing relationship between numbers of intermetallics and rates of D pickup. Intermetallics may provide preferential paths for D diffusion, or result in cracking of the protective oxide film, thus allowing for increased rates of D pickup.

Thus initially, without any decomposition of the beta Zr phase, the Fe may be largely unavailable for intermetallic formation, being tied up in solid solution. There will be relatively few intermetallics present, and D pickup rates will be comparatively low. At this stage, factors other than Fe content, such as concentrations of other less soluble impurity elements, or thermomechanical treatment may play a larger role. This may explain why the increasing relationship between Fe content and D pickup rate is not maintained in the central and inlet regions of the pressure tubes. This may be further complicated by the distribution of impurity

elements along the pressure tubes. Thus, as decomposition of beta Zr proceeds gradually, with the associated rejection of Fe to form intermetallics, rates of D pickup will increase. Accelerations in D pickup rate will occur first at regions close to the outlet. In tubes containing higher concentrations of Fe, the effect will be most pronounced, extending further towards the inlet. This may explain the behaviour of K10, F13 and N16 with respect to D pickup rates versus distance. In J9 the profile of D pickup rate versus distance is quite flat. Possibly in this tube Fe content is sufficiently low that decomposition of the beta Zr has not resulted in rejection of sufficient Fe to result in significant intermetallic formation. Whether J9 would have exhibited increased D pickup rates at the outlet regions after longer in-reactor exposures is an open question. Removal of another pressure tube with similar Fe content, but longer operating times, may provide the answer.

Electron microscopical examinations of samples of removed pressure tubes at regions close to the inlet (50-80 cm), mid-point (290-350 cm) and outlet (490 and 580 cm) could provide more information on changes in tube microstructures occurring in-reactor. Pressure tubes P4K10 and J9 are the prime candidates for such an examination, although inclusion of P4N16 and P3F13 in the program would also be useful. In addition to differences in the amount of decomposition of the beta Zr phase, changes in the distribution of Fe and the size and frequency of intermetallics should be investigated. It may be that all tubes display a similar amount of beta Zr decomposition, although tubes with higher Fe contents may show more intermetallic formation. It is also important to determine the relationship between composition and microstructure of as-installed pressure tubes as a function of axial location, since this may play a role in the observed data as a function of operating time. Examination of available pressure tubes removed from Pickering 8 is recommended to provide this information.

3.3 Data from Bruce Pressure Tubes

The behaviour of Bruce pressure tubes has not been interpreted to the same extent as Pickering tubes. One reason for this is the lack of data on D concentrations at the 580 cm location in X14 and N6 (see Figure 6b). This data should be obtained. D pickup rates show a slight increase with distance and the absence of a distinct tube-to-tube change in slope at the outlet region, possibly because acceleration in D pickup rates have not yet occurred. Generally the ranking of the four Bruce pressure tubes with respect to D pickup is maintained at all distances. There is insufficient spread in Fe content to derive a relationship between Fe concentration and D pickup rate.

3.4 The Linear Model - Conjoint Action of Fe and the Barrier Layer

The alternative explanation we have considered is that rates of D pickup are linear with time. Differences between pressure tubes represents scatter in D pickup rates, with a linear relationship between pickup rates and EFPH for each pressure tube. This scatter has been explained on the basis of Fe content. Explanations of the linear hypothesis based on the influence of Fe content suffer from the fact that this correlation is only valid at regions close to the pressure tube outlet. Possibly this disadvantage may be resolved by hypothesizing conjoint action of Fe and the barrier layer. Viz, Fe may be modifying the behaviour of Zr-2.5 wt% Nb through changes in the barrier layer, a thin layer located at the metal-oxide interface which is relatively impervious to D. The low observed apparent temperature dependence of the rates of D pickup and % theoretical pickup in Figures 6 and 7 could possibly be explained in this way. In J09, with low Fe content, the barrier layer thickness may be increasing with temperature, giving rise to a decreasing relationship between % D pickup and distance. In N16 and F13 with intermediate levels of Fe (just above the threshold level for intermetallic formation), the influence of the barrier layer is reduced. In K10 the effect of the barrier layer is further reduced leading to the

observed high apparent temperature dependence. Thus the influence of Fe itself may be temperature dependent, increasing with increasing temperature and Fe content. This argument does not readily explain the apparent sharp increases in D pickup rates observed close to the outlet ends of P4K10, P4N16 and P3F13.

3.5 Summary

Presently there is insufficient evidence to reach a definitive conclusion to the major question of whether rates of D uptake are accelerating in OH CANDU pressure tubes. This author's judgement is that the accelerating hypothesis has slightly more weight, and can most simply explain both the group and individual behaviour of Pickering pressure tubes. It can also account for the role of precipitate-forming elements such as Fe more readily.

In the analysis presented above, the data has been 'squeezed' to the limit. As stated in Section 1, this author believes this to be necessary in view of the significant implications for major corporate decisions. However, the hazards in 'over-analysing' such limited data from different pressure tubes, should not be overlooked. Variations in environment such as temperature, fluence, and particularly heat transport chemistry and axial variations in pressure tube material, between the various pressure tubes may significantly affect the data.

Given the paucity of data from removed pressure tubes, and the difficulties in interpretation of this data, any predictions of future pressure tube performance for reactor maintenance decisions should be adequately (but not unreasonably) conservative. Unfortunately the issue of linear versus accelerated rates of D pickup is unlikely to be resolved until several further pressure tubes have been removed and possibly the results of critical ongoing research programs are available in the next several years. In order to 'break' the coincidentally increasing relationship between EFPH and pressure tube Fe content, it is recommended that the next pressure tube to be removed contain levels of Fe between 600-700 ppm.

Interpretation of data trends from several removed Zr-2.5 wt% Nb pressure tubes will always be difficult on account of the influences of individual fuel channel chemistries and material composition and thermomechanical processing. Thus, the continued development of an accurate, reliable method for removing innocuous samples from pressure tubes or determination of oxide thickness and D content in-situ is essential.

Further experimental work is ongoing at OHRD and AECL-RC, and in conjunction with the Universities of Toronto, Windsor and MacMaster, to develop an improved understanding of the long-term corrosion and D pickup performance of Zr-2.5 wt% Nb including the effect of pressure tube material.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 Data on oxide thicknesses and D concentrations from removed Zr-2.5 wt% Nb pressure tubes is presented, with interpretations of the data.

4.2 There are two main interpretations of the data. Viz, (i) rates of D pickup have accelerated in Pickering pressure tubes P4K10, P3F13 and P4N16, or (ii) rates are linear, and differences between pressure tubes reflect scatter in the data probably as a result of differences in pressure tube material. Each of these interpretations leads to quite different predictions, and implications for reactor maintenance decisions.

4.3 Equivalent H levels predicted for REFAB in Pickering 3 and 4 pressure tubes by 1995 and 2000 are 45 and 72 ppm respectively, assuming initial H levels of 10 ppm. These predictions are well above levels required for blister formation. For these predictions, rates of D pickup are assumed to accelerate to a higher linear rate of 10.5 ppm/annum after 122 000 EFPH. Assuming linear rates of D pickup with operating time, predictions of equivalent H are below that required for blister formation until at least 1995.

4.4 Pressure tube data is extremely limited, and there is a lack of fundamental understanding of long-term corrosion and D pickup processes in Zr-2.5 wt% Nb. Based on discussions with colleagues and review comments for this report, it is generally believed that it is not possible to reach firm conclusions or assign probabilities to either of the above interpretations. However, it is this author's judgement that the accelerating hypothesis is slightly more probable.

4.5 Decomposition of the beta Zr phase occurring after long in-reactor exposures, may lead to rejection of Fe to form intermetallics which in turn results in accelerations in D pickup rates. A threshold level of Fe of 600 ppm for Pickering pressure tubes, may exist below which accelerated D pickup does not occur. This hypothesis may account for the effect of Fe content on D pickup rates, and the significant increases in D pickup rates observed in outlet regions. Electron microscopical examinations of samples of removed Pickering pressure tubes are recommended to provide more information on changes in tube microstructures occurring in-reactor.

4.6 Possible conjoint action of Fe and the barrier layer may explain deficiencies in the linear D pickup model. However, it does not readily explain the apparent sharp increases in D pickup rates observed close to the outlet ends of P4K10, P4N16 and P3F13.

4.7 In order to 'break' the coincidentally increasing relationship between EFPH and pressure tube Fe content, it is recommended that the next pressure tube to be removed from Pickering 3 or 4 contain levels of Fe between 600-700 ppm.

4.8 Analysis of data from different pressure tubes is complicated by differences in individual fuel channel chemistries and material composition and thermomechanical processing. Thus, the continued development of an accurate, reliable method for removing innocuous samples from pressure tubes or determination of oxide thickness and D content in-situ is essential.

4.9 It is recommended that analysis of pressure tubes removed from Pickering 8 be performed to determine changes in composition and microstructure as a function of axial location for as-installed tubes.

4.10 Interpretation of data from Bruce pressure tubes has been limited by the lack of data on D concentrations at the 580 cm location in X14 and N6. It is recommended that further data should be obtained.

4.11 Further experimental work is ongoing at OHRD and AECL-RC, and in conjunction with the Universities of Toronto, Windsor and MacMaster, to develop an improved understanding of the long-term corrosion and D pickup performance of Zr-2.5 wt% Nb including the effect of pressure tube material.

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REFERENCES

1. B.D. Warr, A.H.C. Chan and S.R. Lukac, "Modelling Corrosion and Deuterium Pickup in Operating Reactor Pressure Tubes, OHRD Report No 86-151-K, July 21, 1986.

2. B.D. Warr and M.W. Hardie, "Predictions of Equivalent Hydrogen Levels in Pickering 3 and 4 Pressure Tubes", Memorandum to Refab Task Force, File 827.22, October 2, 1986.

3. B.D. Warr, "Predictions of Corrosion and Deuterium Pickup in Darlington Pressure Tubes", Memorandum to M.W. Hardie, File 827.22, November 3, 1986.

4. K. Hollings and B.D. Warr, "Computer Data Base of Literature on Zirconium Corrosion and Hydrogen Pickup", OHRD Report M86-119-K.

5. B. Cox, "Long-Term Oxidation of Zr-2.5 wt% Nb Alloy", AECL Report #5610, September, 1976.

6. D. Lim, N.A. Graham and D.O. Northwood, "The Degradation of Zirconium Alloys in Nuclear Reactors - A Review", Atomic Energy Control Board Research Report, January 23, 1986.

7. D. Northwood, Private Communication, November 1986.

8. B.D. Warr and S.R. Lukac, Review of Discussions with AECL-RC Staff", OHRD Report No M85-122-K, November 25, 1985.

9. B. Cox, "Extrapolation of PT D Data", AECL Memorandum to B.D. Warr, December 9, 1986.

10. V.F. Urbanic, AECL Memorandum to B.A. Cheadle, April 17, 1986.

11. R.G. Barton, Memorandum to Distribution, File NCCF 4.6, April 22, 1986.

12. R.A. Ploc, AECL Memorandum to B.A. Cheadle, May 27, 1986.

13. V.F. Urbanic, Memorandum to B.A. Cheadle, October 21, 1986.

14. C.D. Cann and R.C. Styles, AECL Report No WNRE-610, August 1984.

15. M.W. Hardie, "ASTM 92 Accelerated Corrosion Tests", OH Memorandum, File 907-N31100P, November 19, 1986.

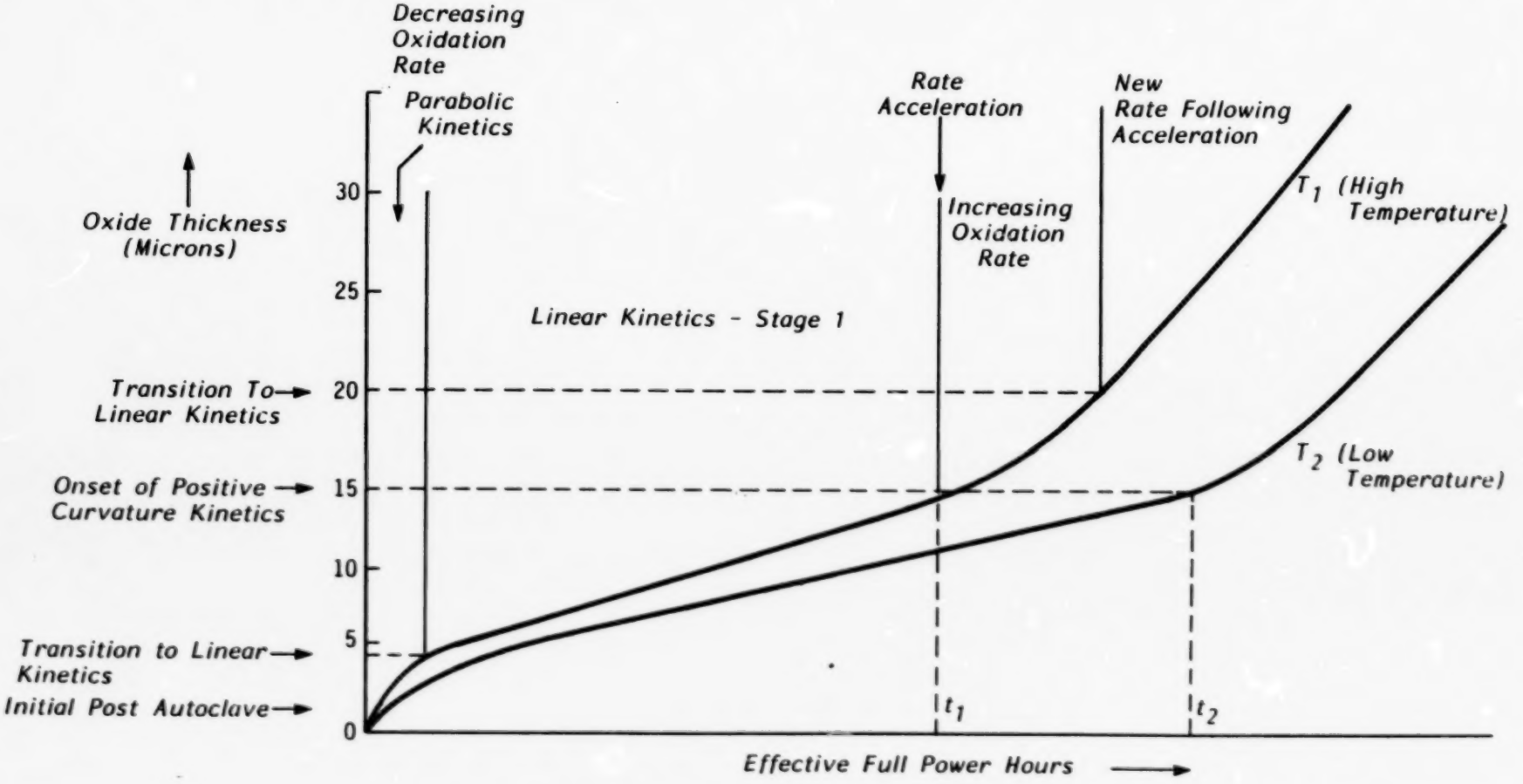

FIGURE 1

SCHEMATIC OF MOST PROBABLE RELATIONSHIP OF OXIDE THICKNESS VS EFFECTIVE FULL POWER HOURS FOR Zr-2.5 wt% Nb PRESSURE TUBES (FOR 2 TEMPERATURES WHERE $T_1 > T_2$. ONSET OF BREAKAWAY OXIDATION OCCURS AT t_1 & t_2)

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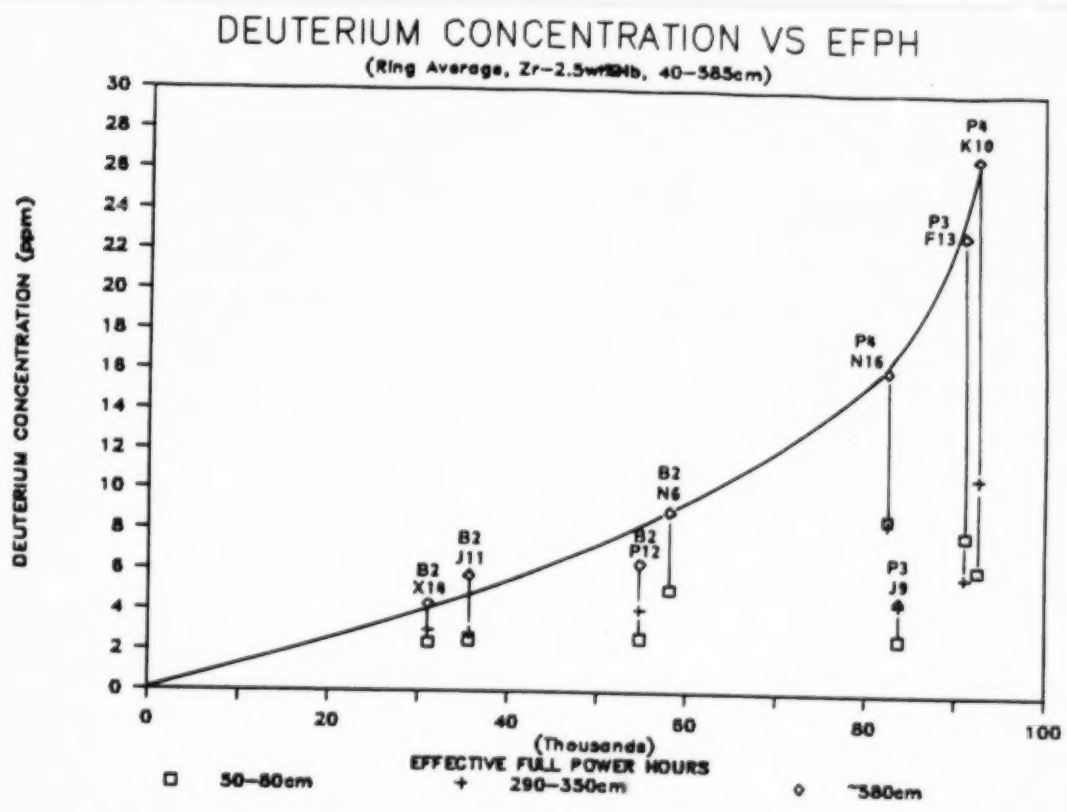

FIGURE 2a

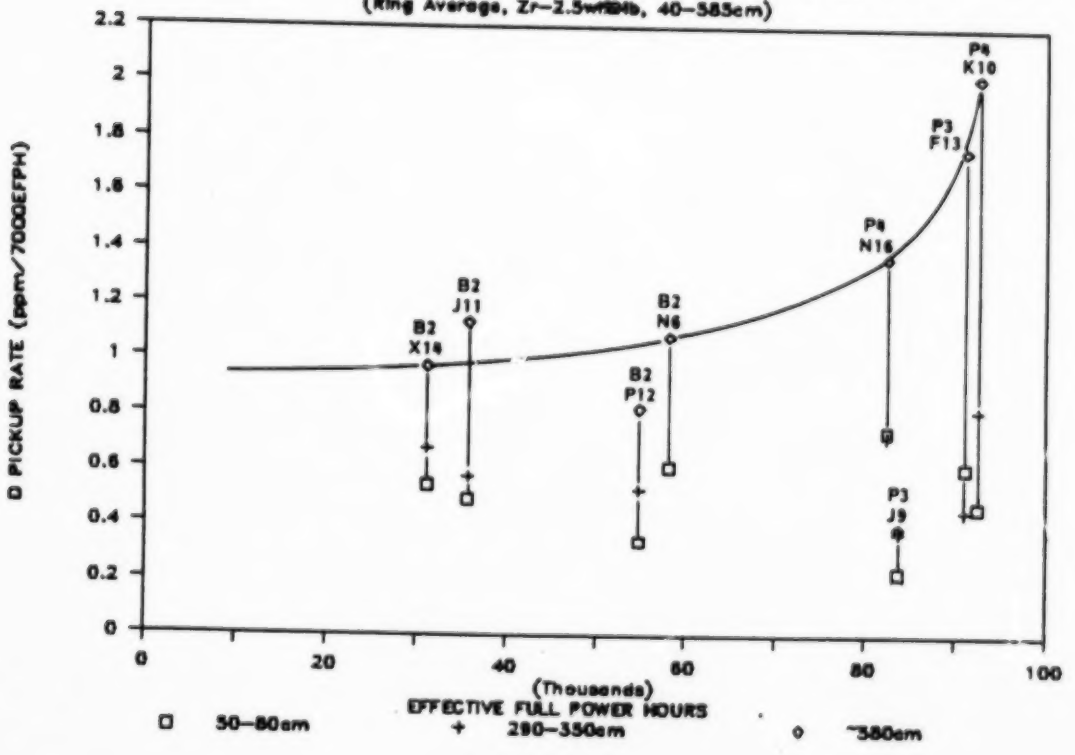

FIGURE 2b

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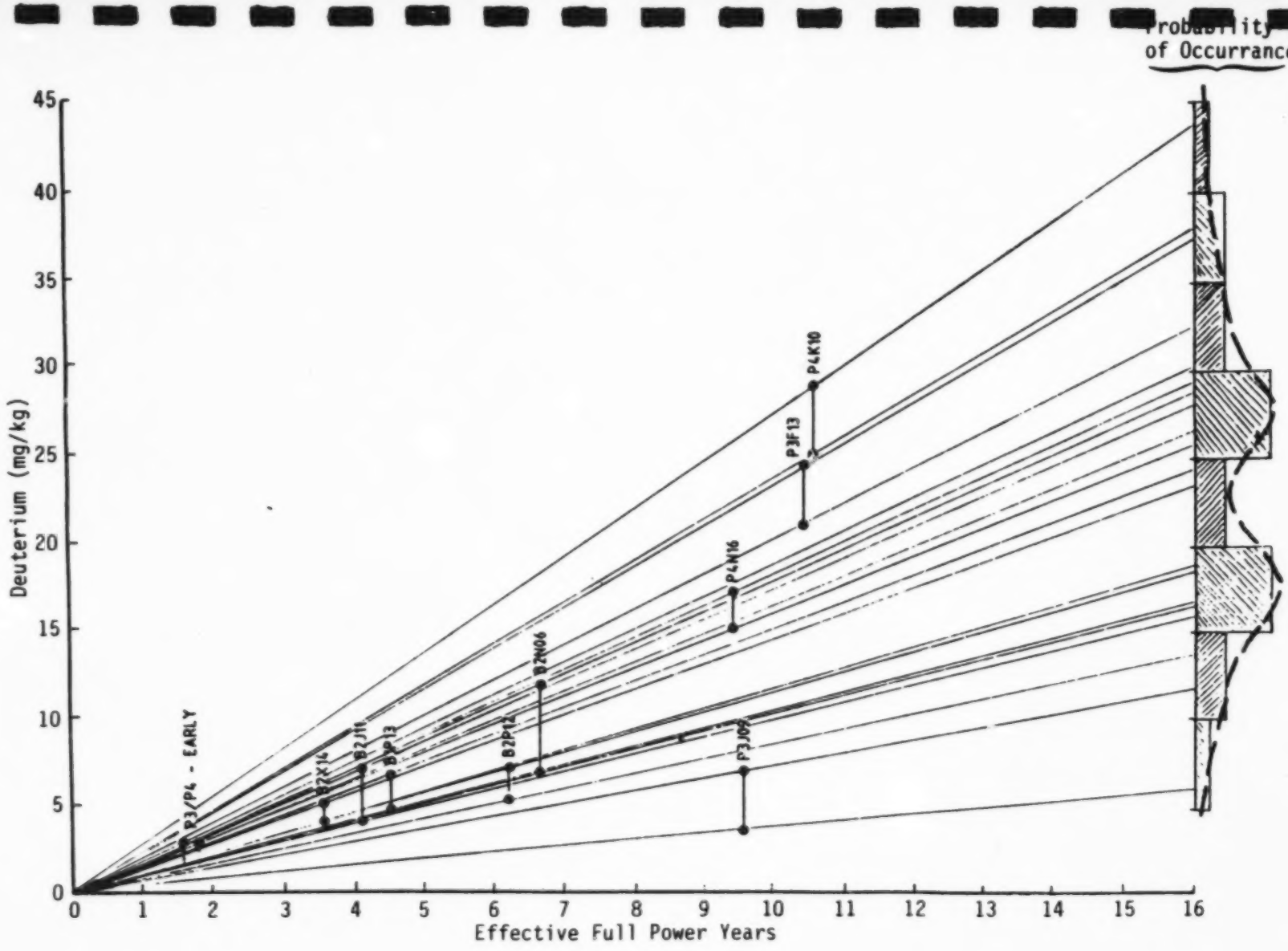
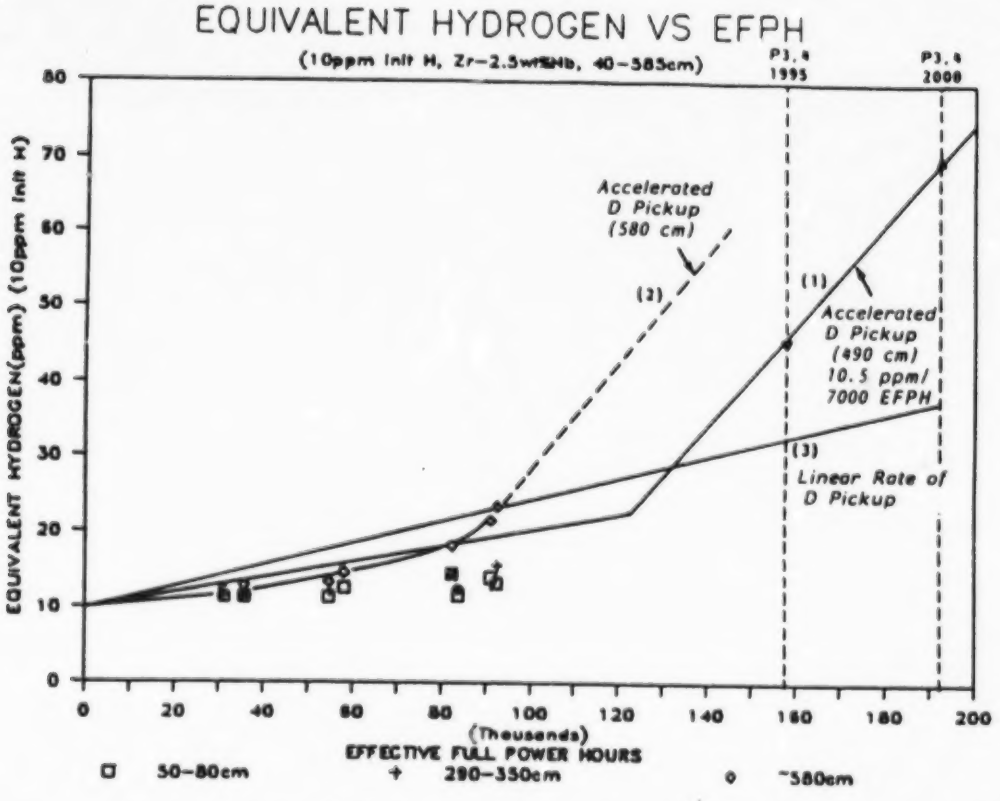


FIGURE 2c

LINEAR EXTRAPOLATION OF DEUTERIUM CONCENTRATION VERSUS EFPH
(FROM REFERENCE 9)

174403-RD



(▽▲ Predictions for Pickering 3 & 4 Pressure Tubes by 1995 & 2000 Assuming Accelerated D Pickup)

FIGURE 3a

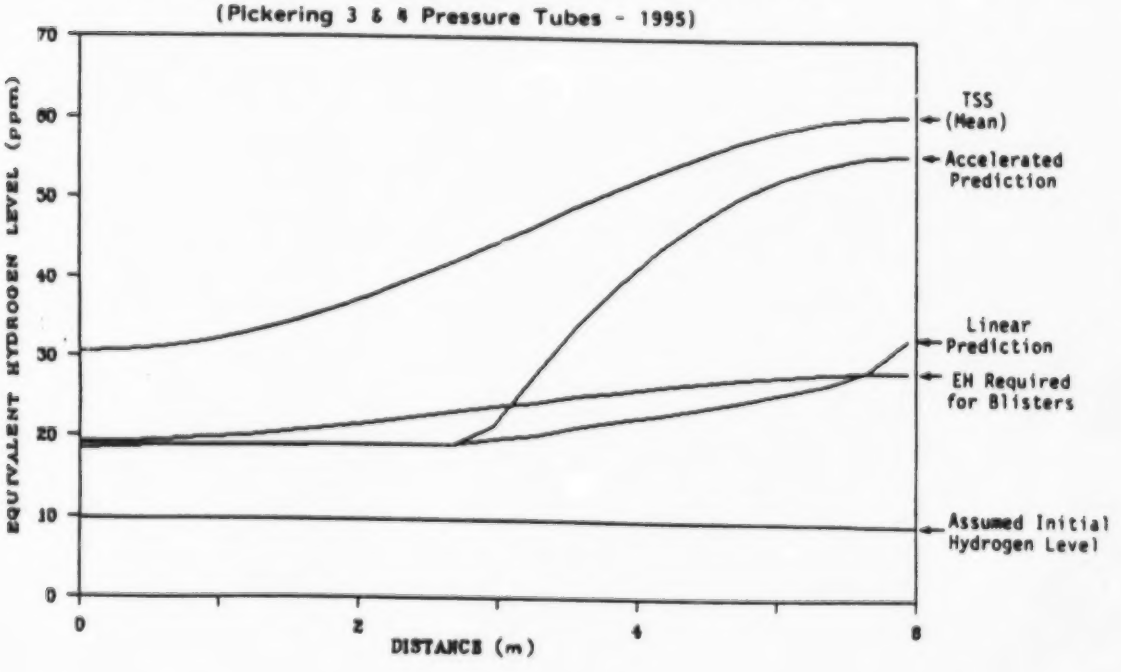


FIGURE 3b

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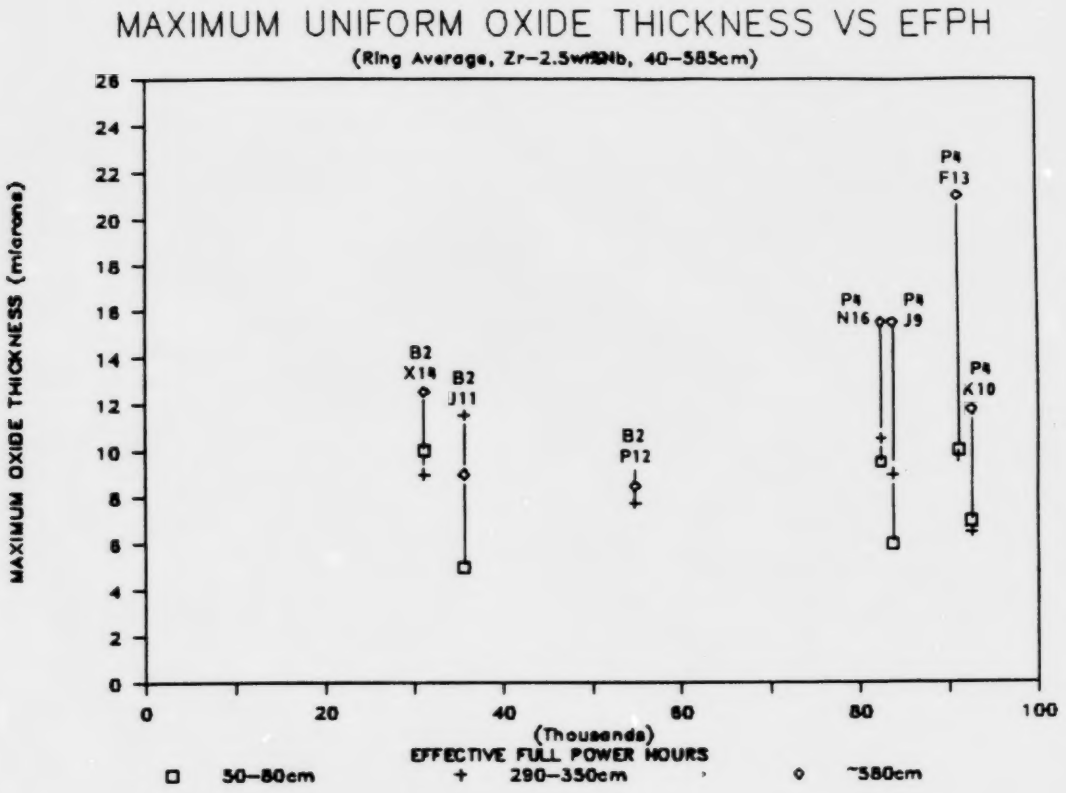

FIGURE 4a

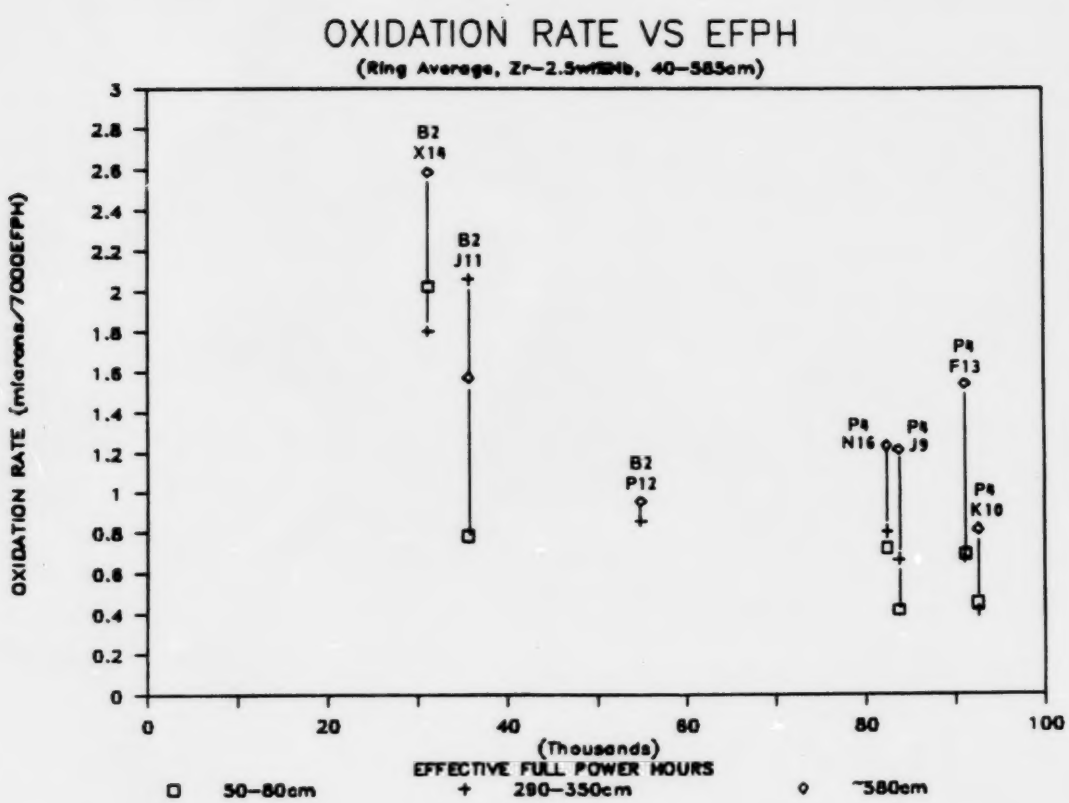

FIGURE 4b

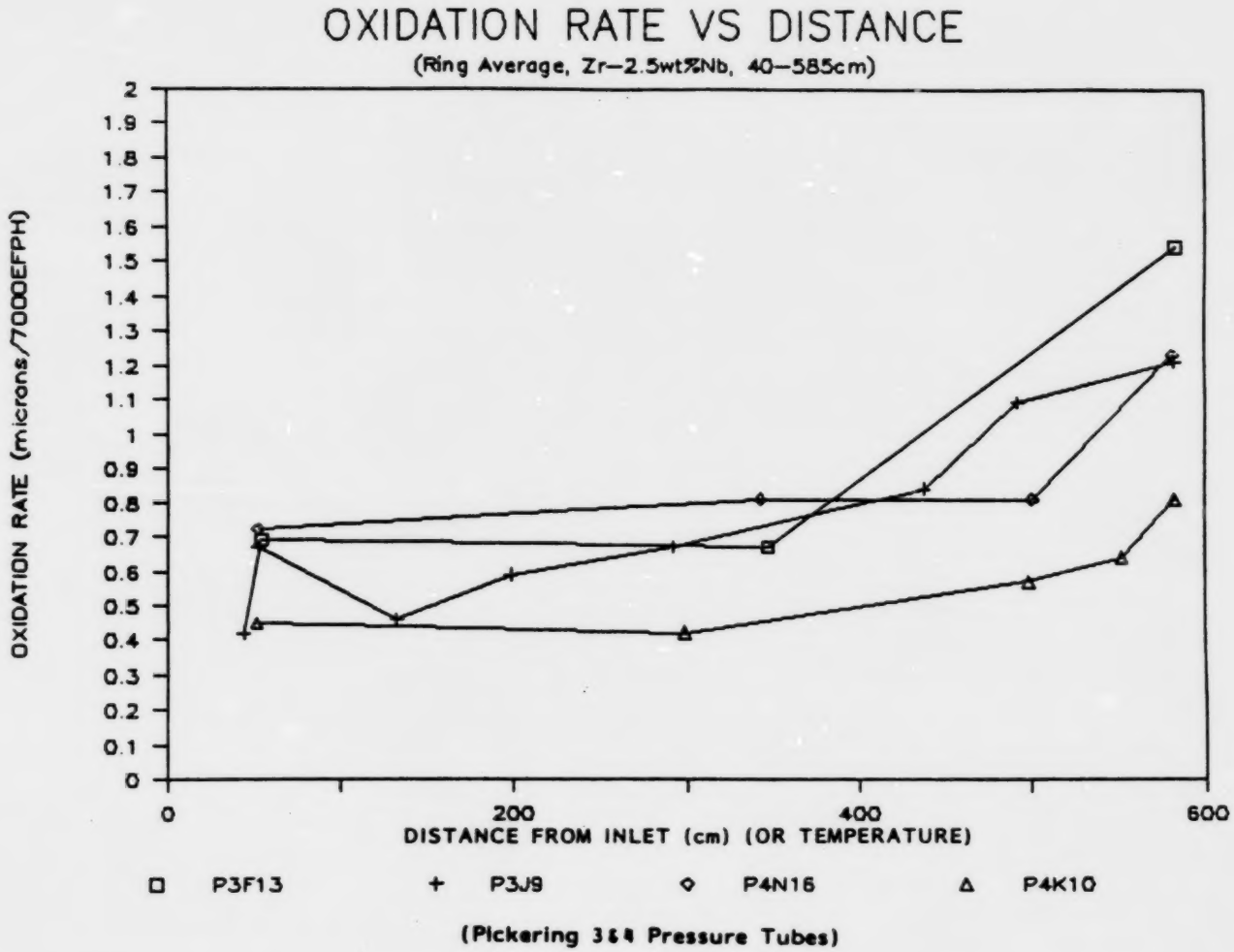

FIGURE 5

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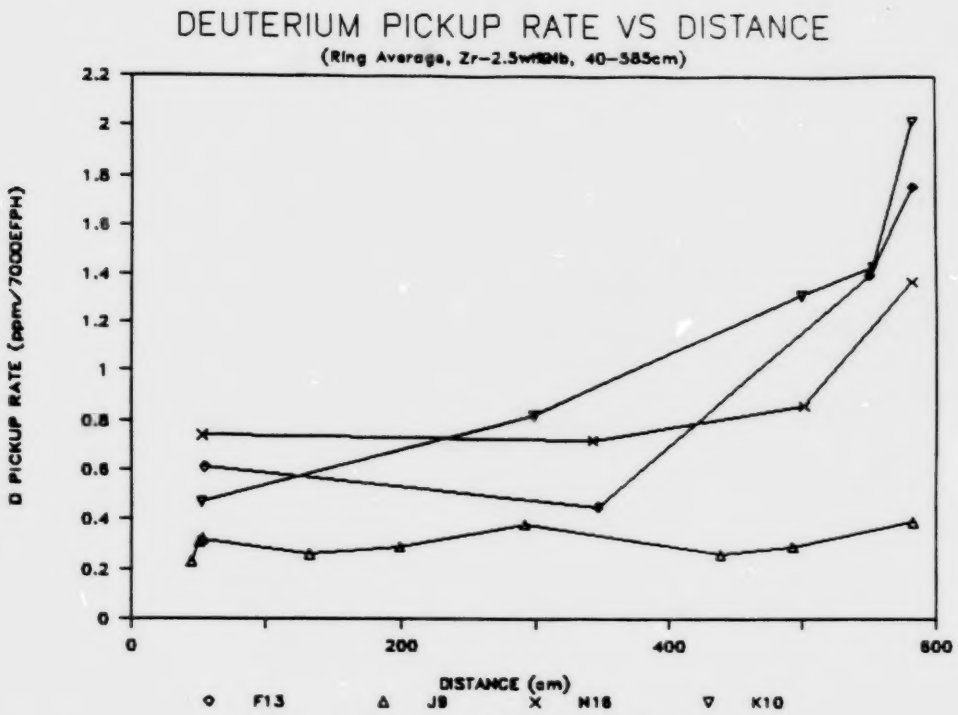
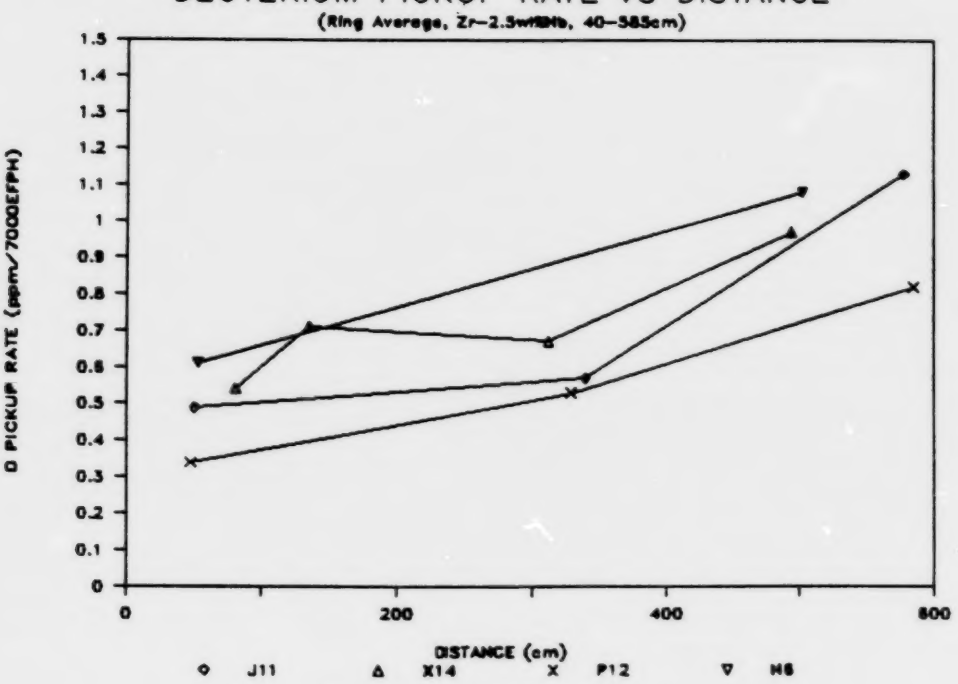


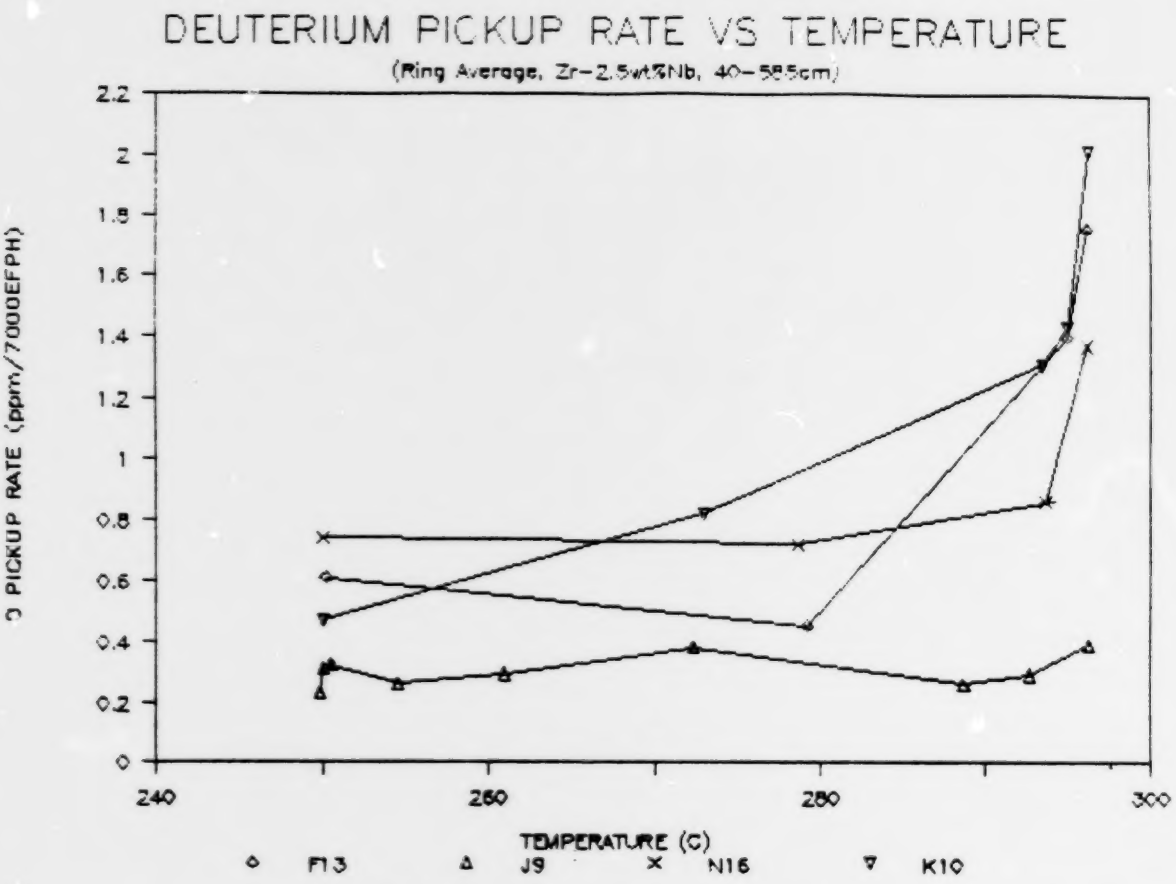
(Pickering 3 & 4 Pressure Tubes)

FIGURE 6a



(Bruce 2 Pressure Tubes)

FIGURE 6b



(Pickering 3 & 4 Pressure Tubes)

FIGURE 6c

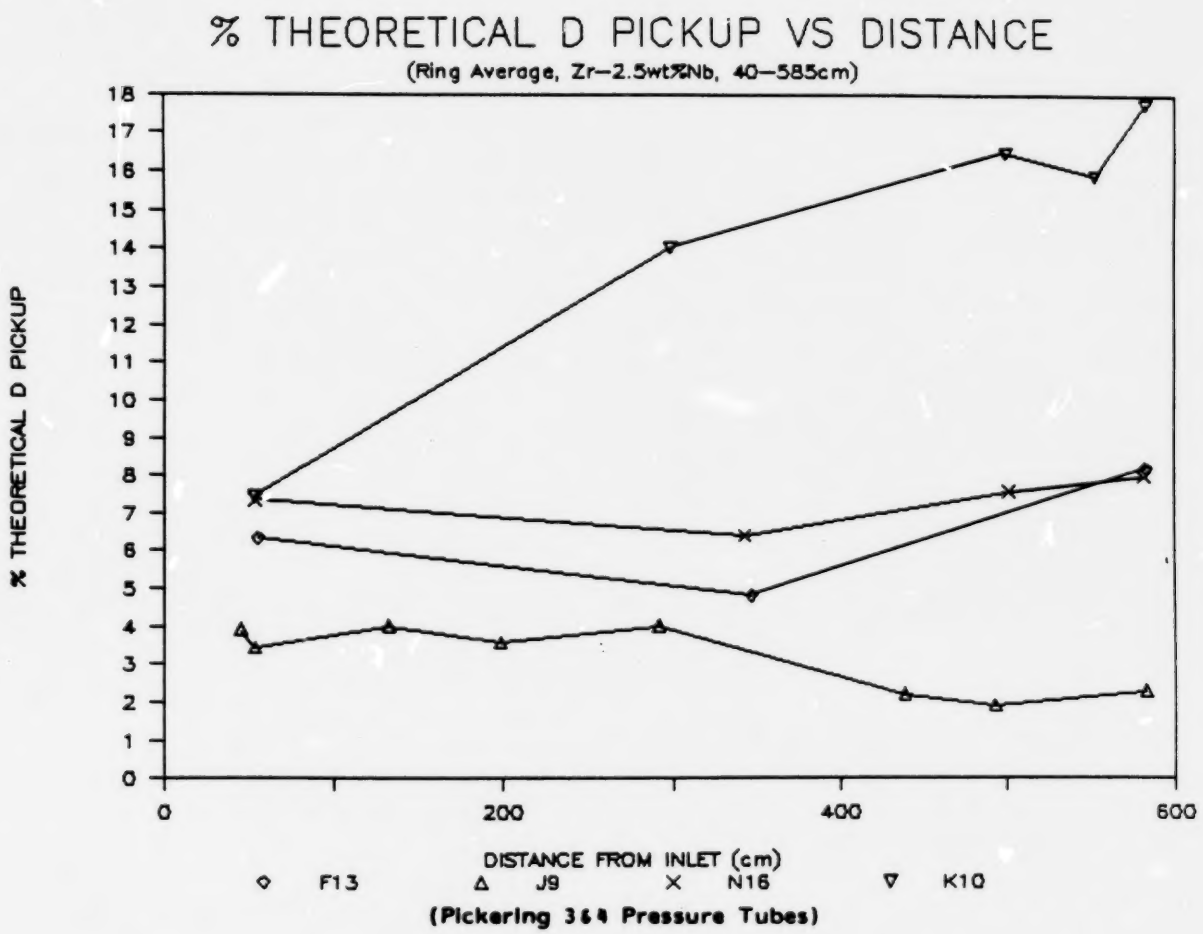


FIGURE 7

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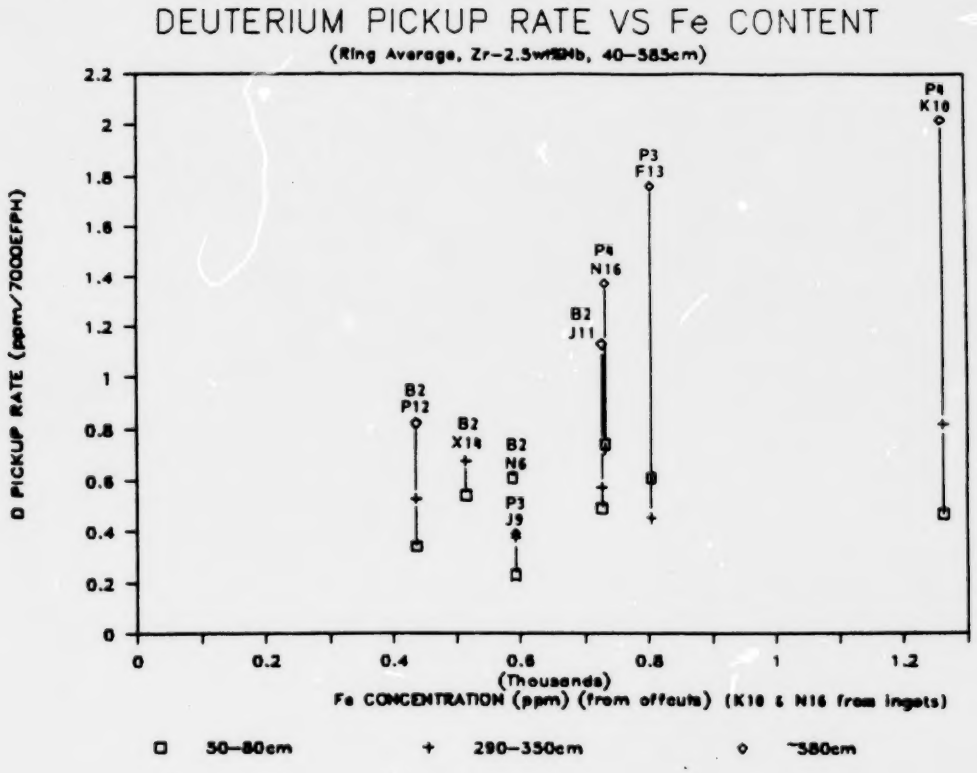


FIGURE 8a

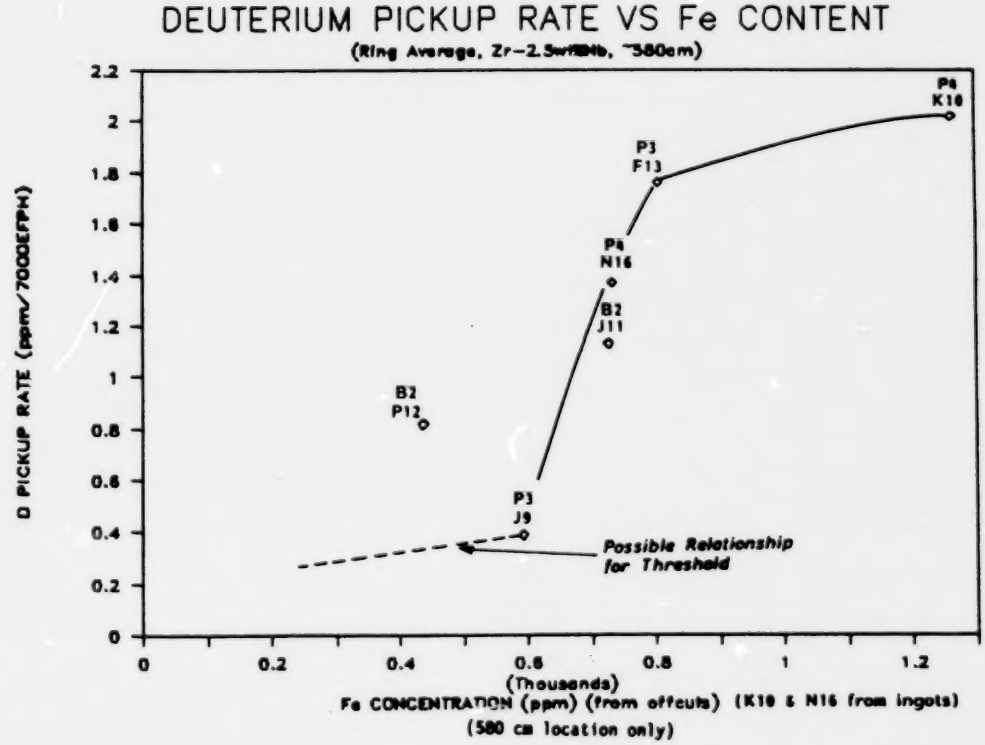


FIGURE 8b

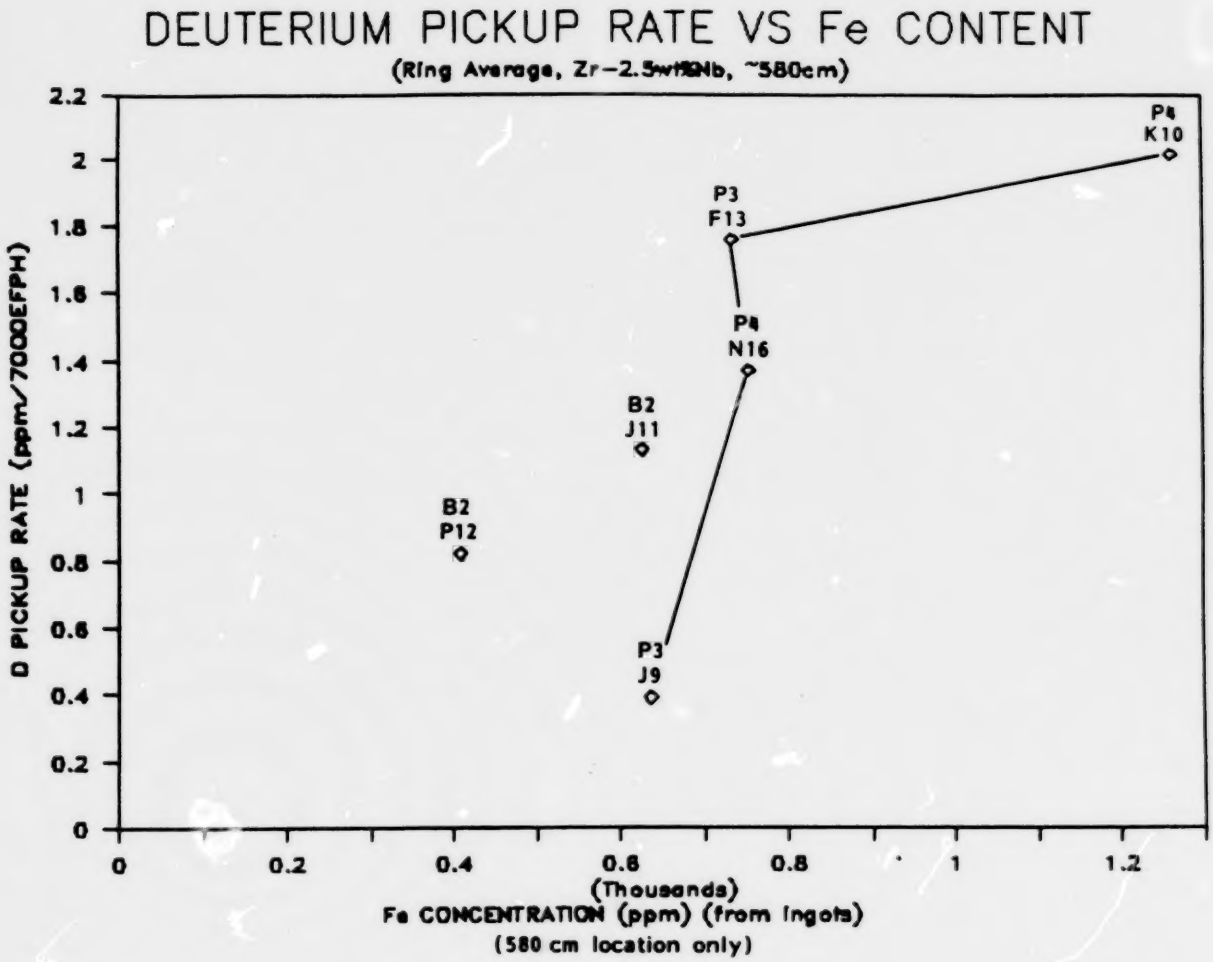


FIGURE 8c

173495 RD

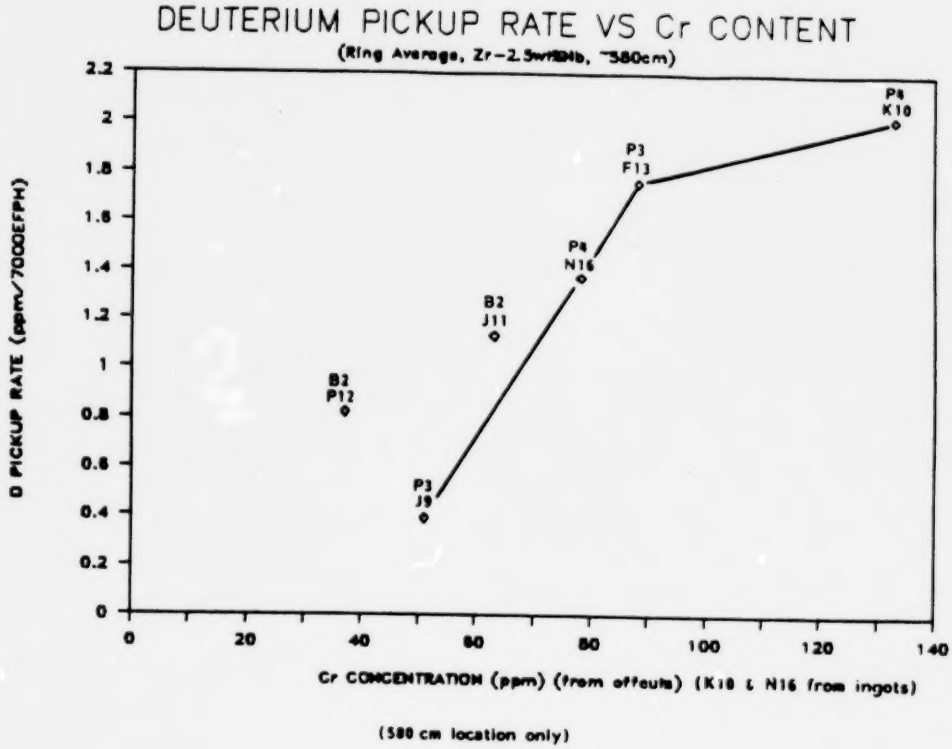


FIGURE 9a

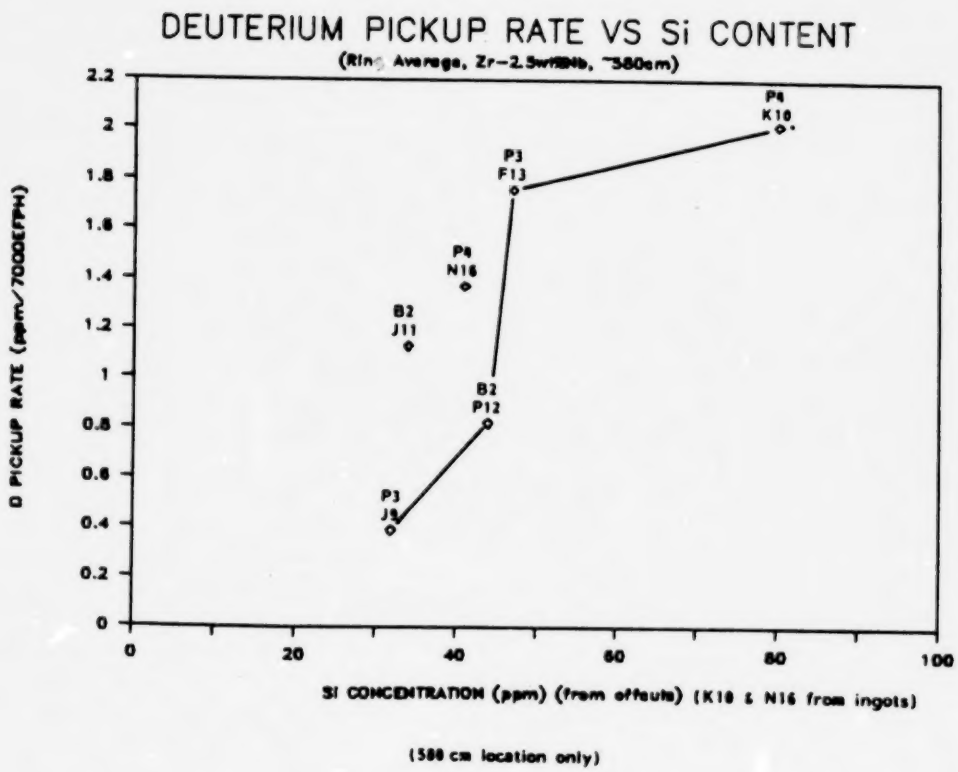


FIGURE 9b

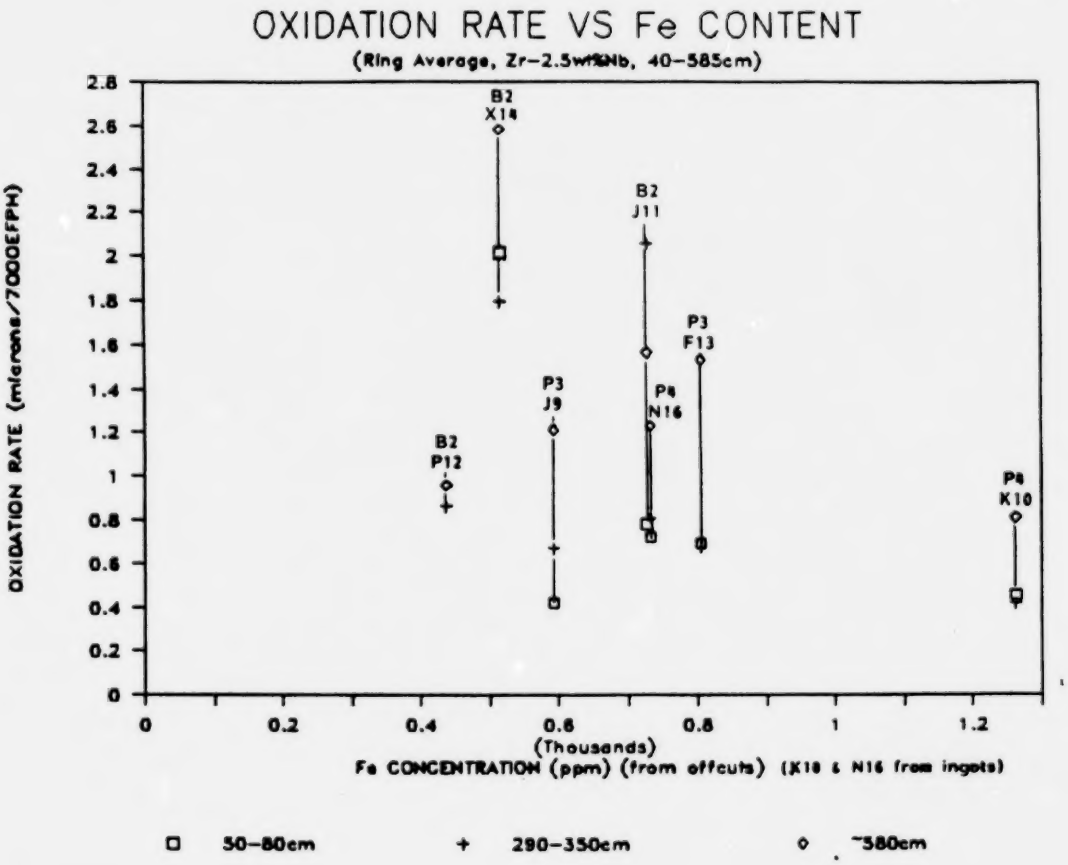
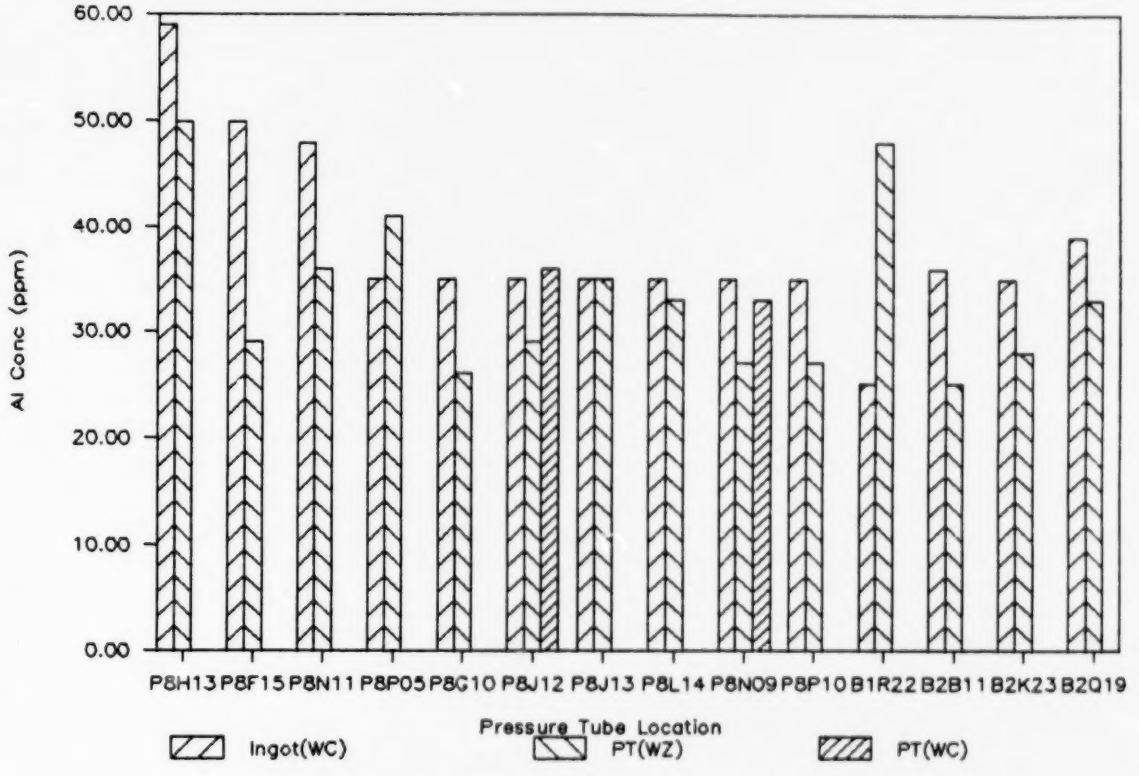

OXIDATION RATE VS Fe CONTENT
(Ring Average, Zr-2.5wt%Nb, 40-585cm)
OXIDATION RATE (microns/7000EFPH)
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
B2 X14
B2 J11
P3 F13
P3 J9
P8 N16
B2 P12
P8 K10
0
0.2
0.4
0.6
0.8
1
1.2
(Thousands)
Fe CONCENTRATION (ppm) (from offcuts) (X18 & N16 from ingots)
50-80cm
290-350cm
~580cm

FIGURE 10

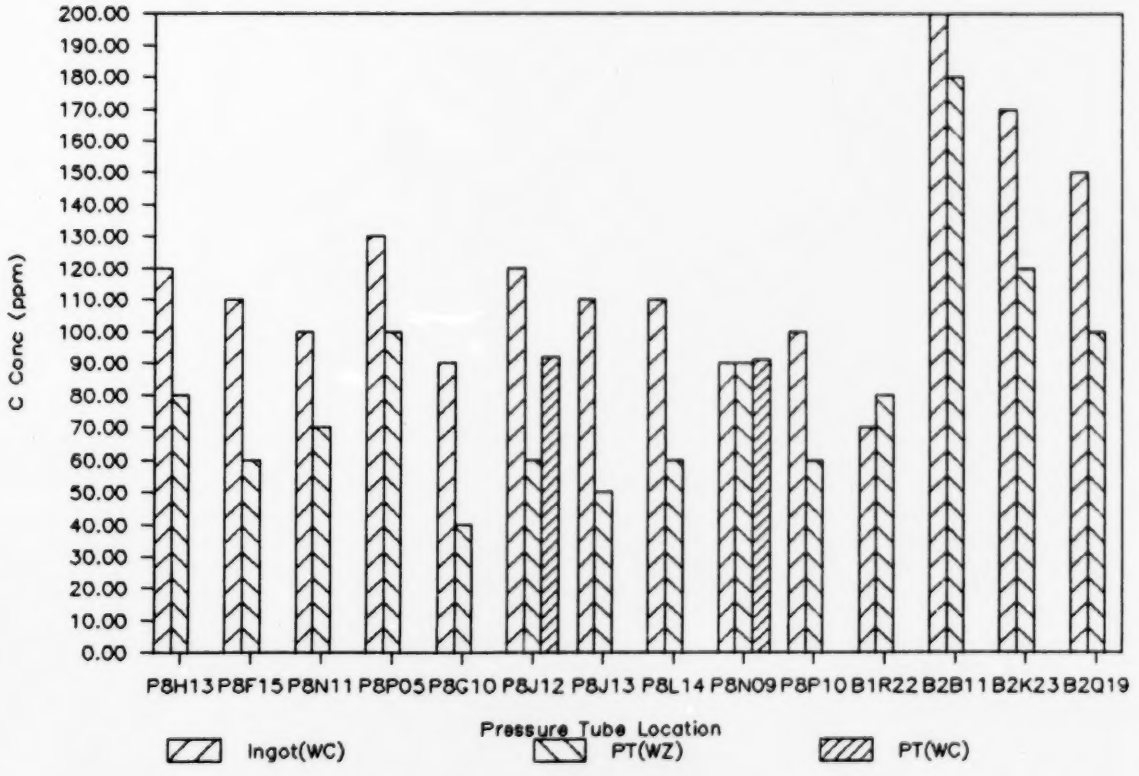
APPENDIX 1

COMPARISON OF ANALYSES OF TRACE IMPURITIES IN SAMPLES OF PRESSURE TUBES AND OFFCUTS

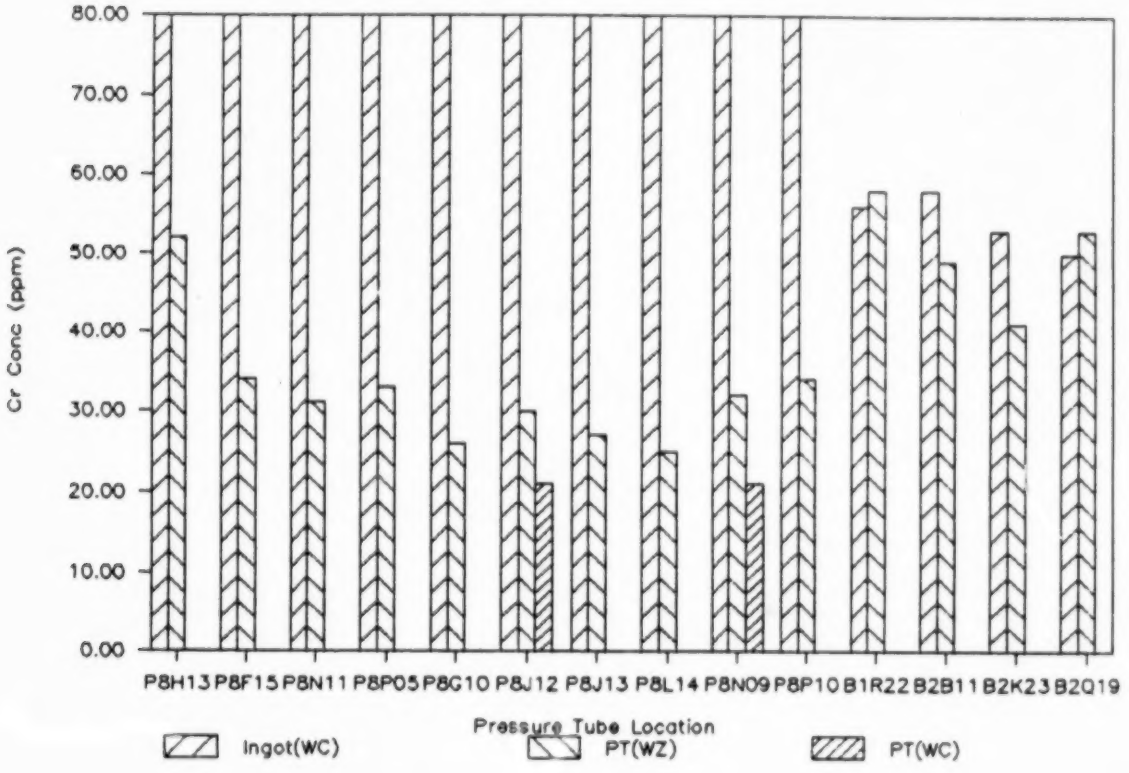
COMPARISON OF ANALYSES – Al



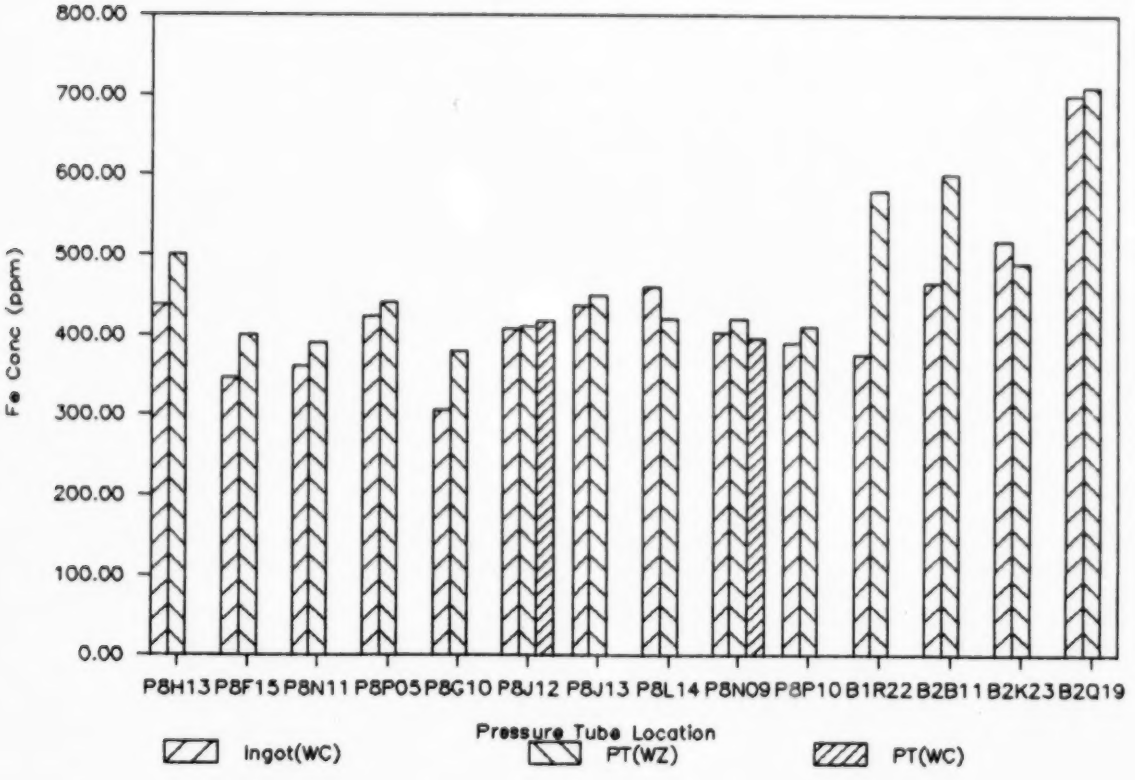
COMPARISON OF ANALYSES – C



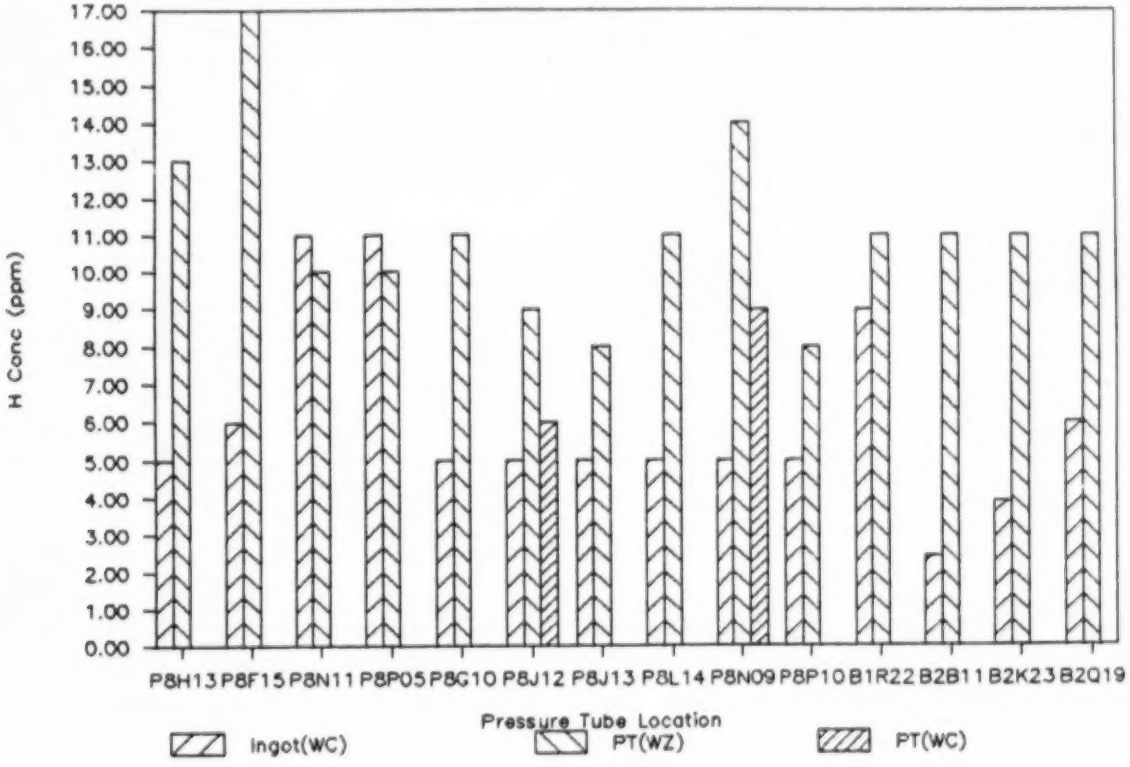
COMPARISON OF ANALYSES – Cr



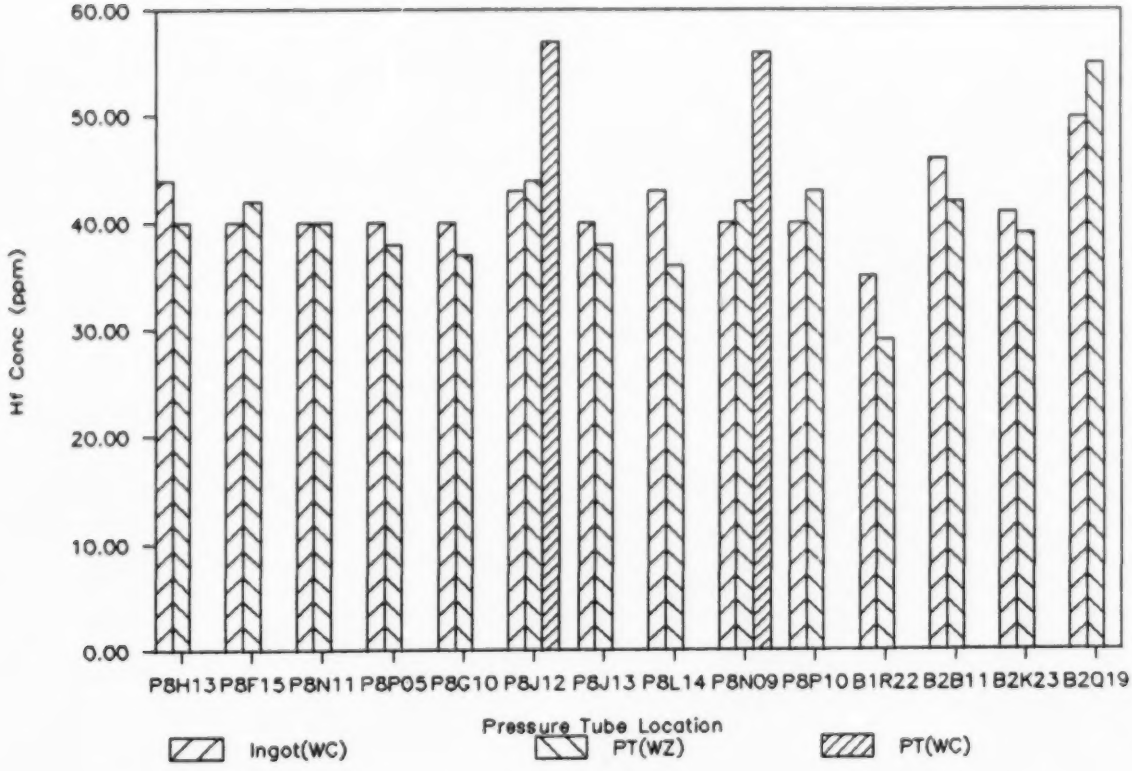
COMPARISON OF ANALYSES – Fe

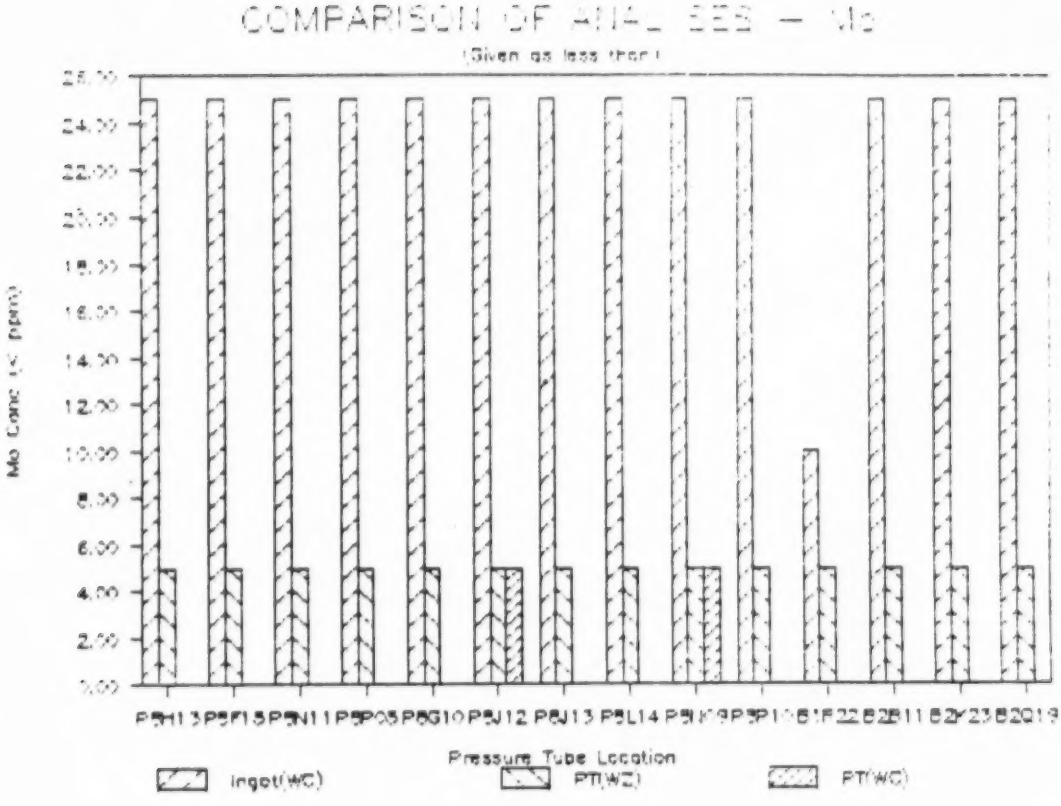


COMPARISON OF ANALYSES – H

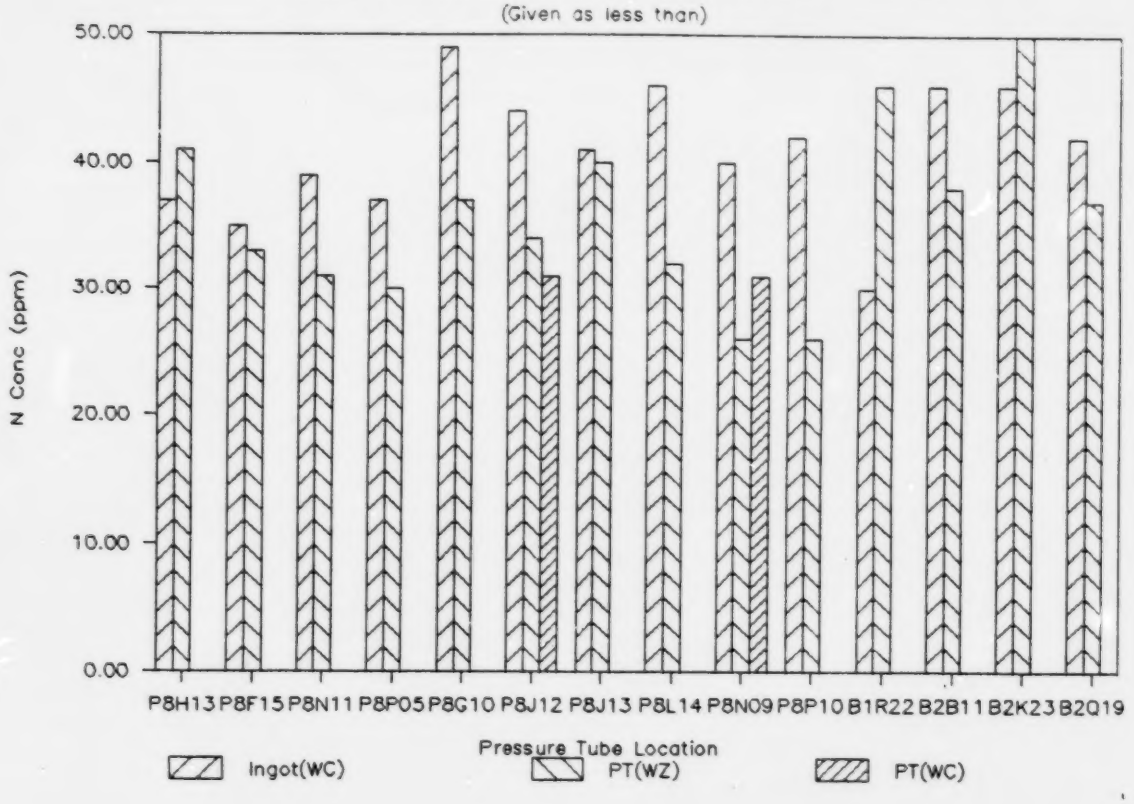


COMPARISON OF ANALYSES – Hf

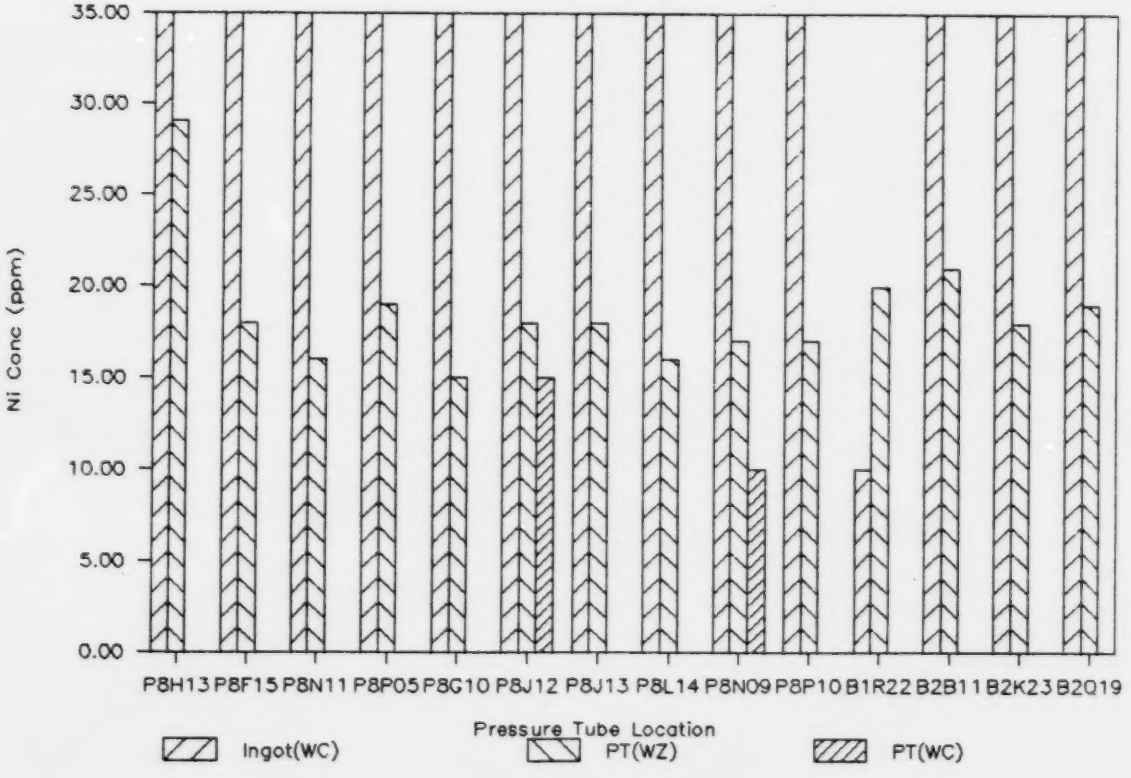



COMPARISON OF AVAL SEG — Mo
(Given as less than)
Mo Conc (x, ppm)
Pressure Tube Location
Ingot(WC)
PT(WZ)
PT(WC)

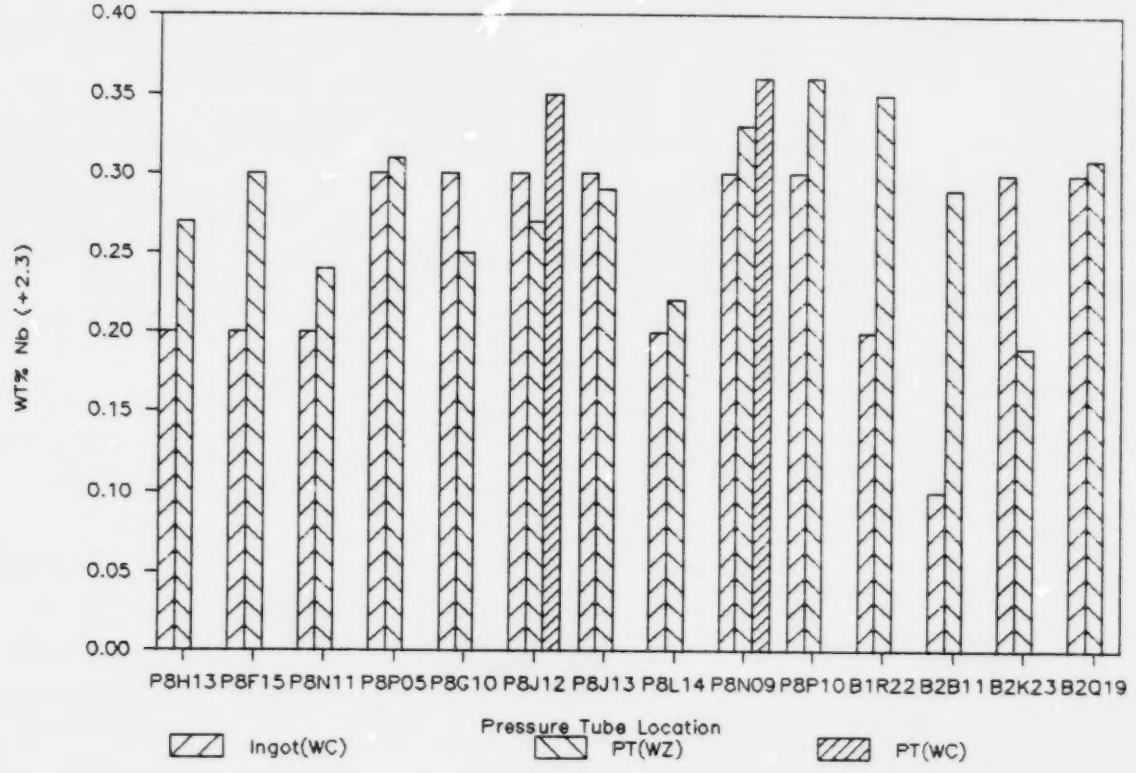
COMPARISON OF ANALYSES – N



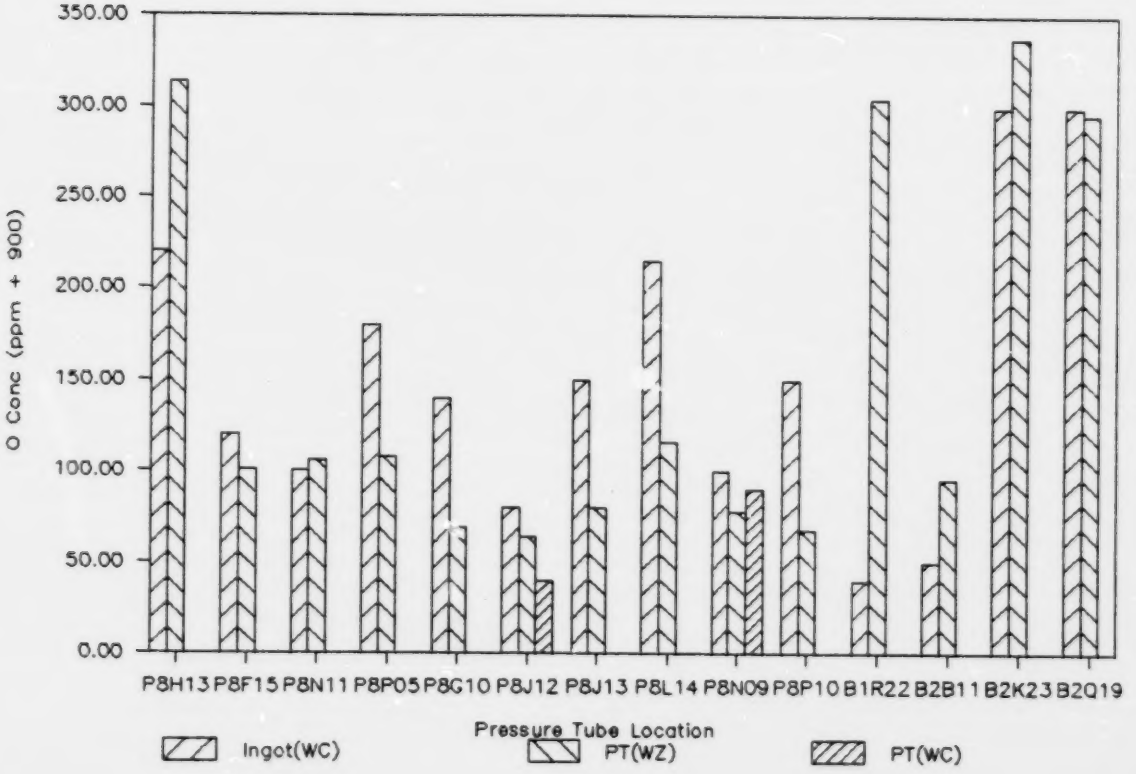
COMPARISON OF ANALYSES – Ni



COMPARISON OF ANALYSES – Nb

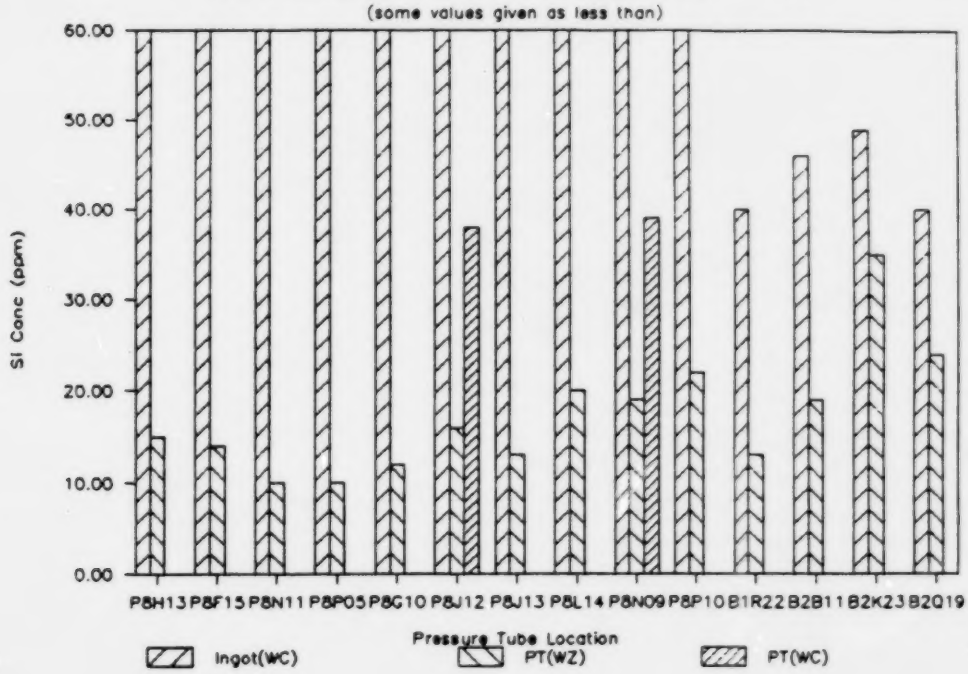


COMPARISON OF ANALYSES – O



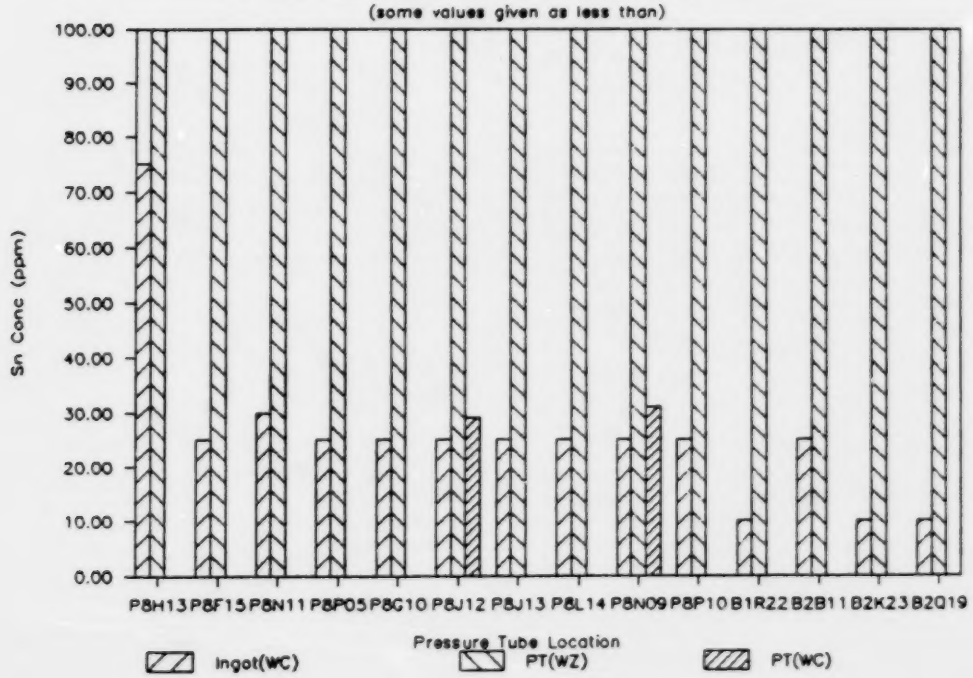
COMPARISON OF ANALYSES – Si

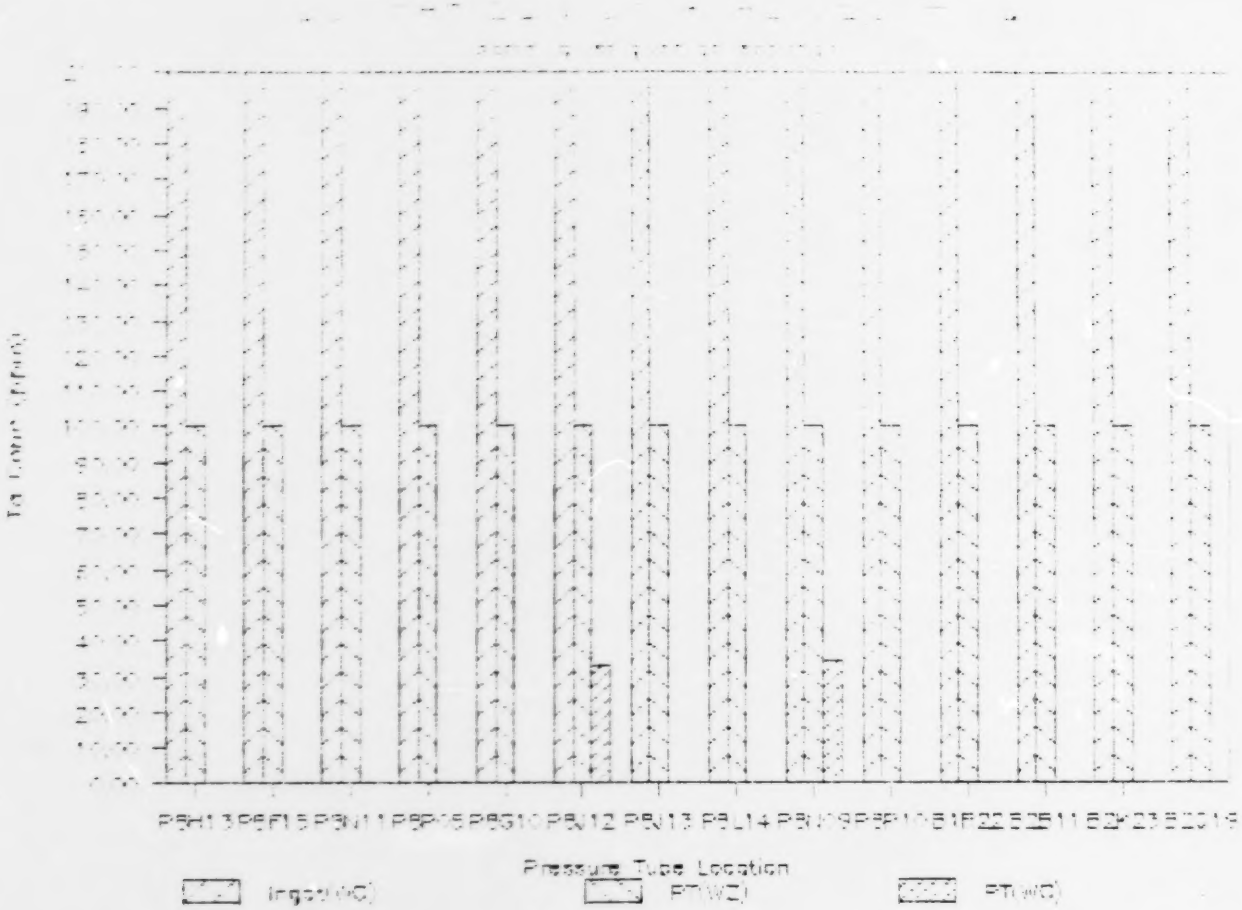
(some values given as less than)



COMPARISON OF ANALYSES – Sn

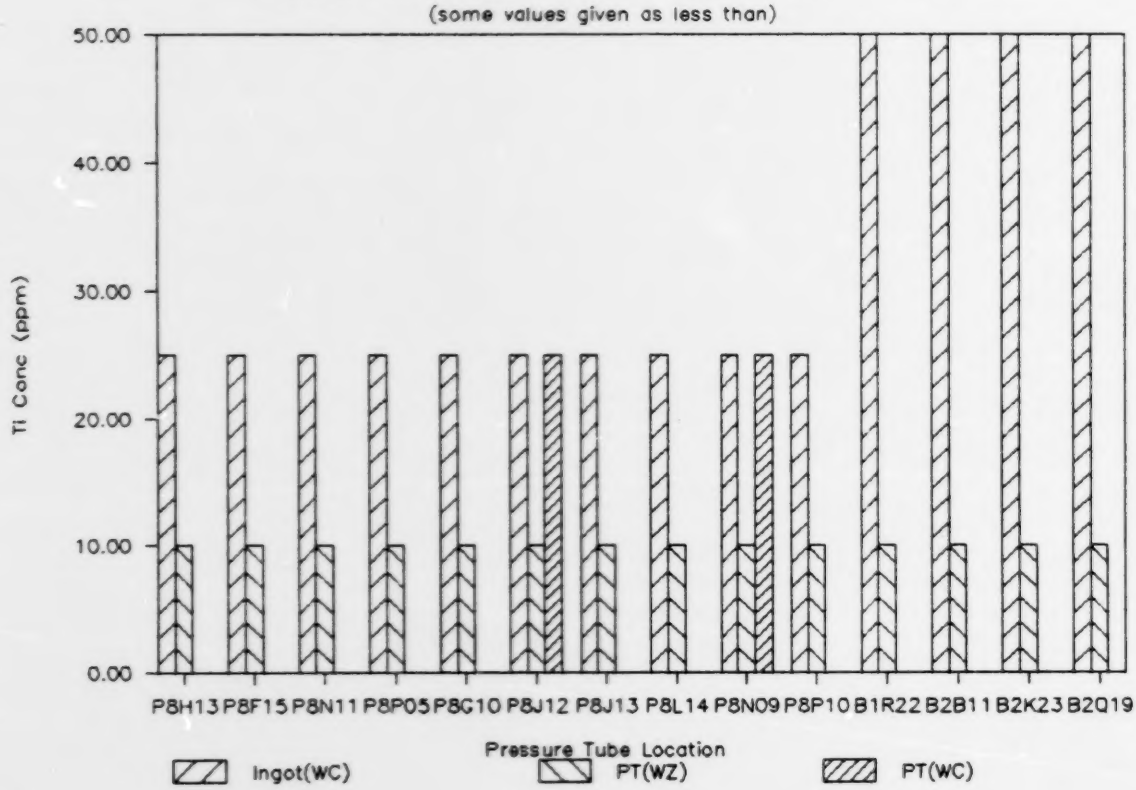
(some values given as less than)





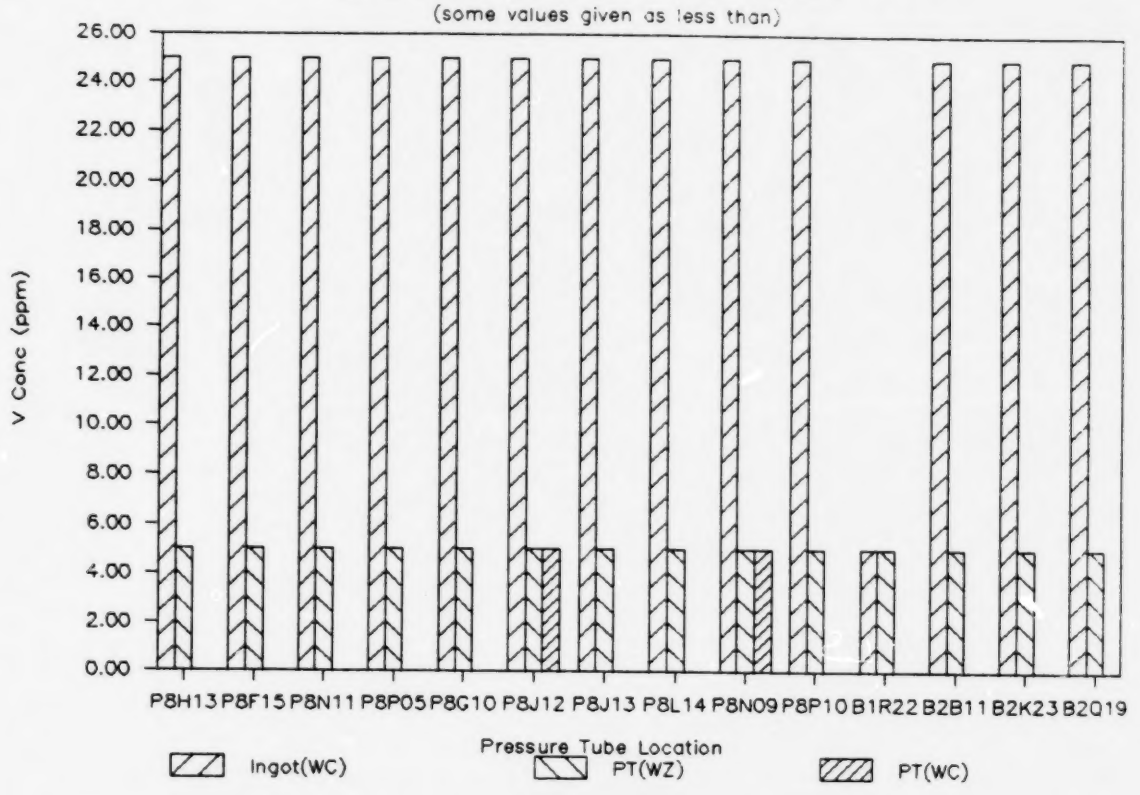
COMPARISON OF ANALYSES – Ti

(some values given as less than)



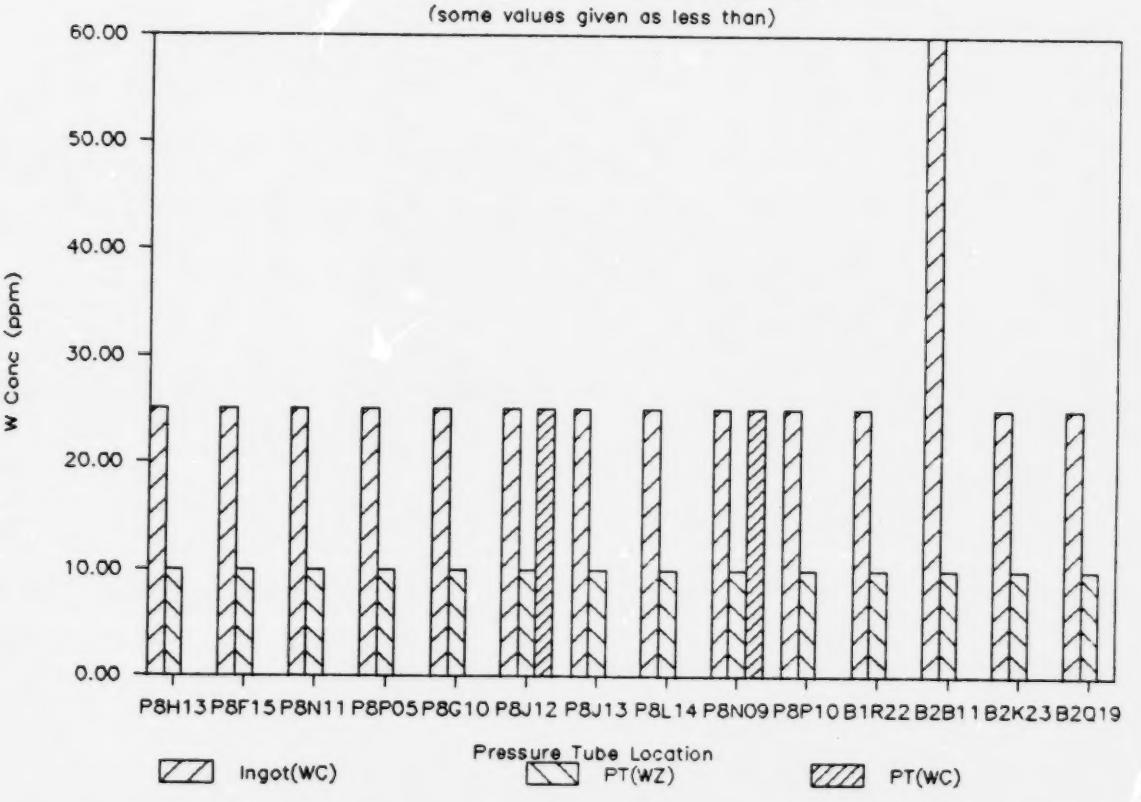
COMPARISON OF ANALYSES – V

(some values given as less than)



COMPARISON OF ANALYSES – W

(some values given as less than)



APPENDIX 2

PROGRESS REPORT ON MICROSTRUCTURAL ANALYSIS OF Zr-2.5 wt% Nb

X.Y. MENG, D.O. NORTHWOOD, UNIVERSITY OF WINDSOR

MICROSTRUCTURAL ANALYSIS OF Zr-2.5wt%Nb

PROGRESS REPORT NO. 1

FOR PERIOD ENDING

NOVEMBER 28, 1986

by

Xianying Meng and Derek O. Northwood
Department of Engineering Materials
University of Windsor
Windsor, Ontario
N9B 3P4

November 1986

MICROSTRUCTURAL ANALYSIS OF Zr-2.5wt%Nb

INTRODUCTION

In the initial period of research grant, we have examined a total of 11 different materials; 9 samples of tubing in the as-received condition and 2 samples from tubing that had been annealed by Ontario Hydro in order to remove/reduce the high dislocation density and thus facilitate the identification of the intermetallic precipitates.

Up to 10 thin foils were prepared from each sample. The total number of foils prepared from each tube sample and the number of 'good' foils (i.e., those having reasonably large thin areas reasonably free from oxidation and polishing/preparation artefacts) are given in Table 1. The foils were examined principally by transmission electron microscopy (TEM) techniques but scanning electron microscopy (SEM) was also used to compare the grain sizes and distribution of the β-phase.

MICROSTRUCTURAL OBSERVATIONS

(i) Grain Size and General Microstructural Features

The general microstructure, size and shape of the grains are shown in Figure 1 by the representative SEM micrographs of samples Q19, B11, K23 and R22. The microstructure consists of long elongated α-Zr grains bounded by filaments of the β-phase. The SEM micrographs are extremely useful for grain size and shape determinations but do not provide information of other microstructural features such as dislocation density. TEM micrographs of all 9 as-received samples (i.e., not annealed) are given in Figure 2. The TEM micrographs show that all tubes contained a high dislocation density (it is probably worth noting that even after annealing there were many dislocations present in the microstructure). Given the very high dislocation density, then thin foil TEM techniques

would not be particularly useful in identifying differences in dislocation density between the different tubes. Rather an x-ray line broadening technique would be recommended. Differences in dislocation density give rise to differences in stored energy and changes in chemical reactivity.

Based on the SEM and TEM observations, the tubes were placed into 3 groups according to grain size as measured by the thickness of the elongated α-grains. Table 2 lists the 9 tubes in order of grain size. The grain sizes are described in qualitative terms as large, medium or small. On the advice of Ontario Hydro personnel, quantitative grain size measurements were not made at this time. The reasons for this decision were (i) at this stage, we were primarily concerned with identifying any intermetallic precipitates and (ii) the grain size depends markedly on the position in the extruded tube with factors of two or more differences being found between back and front ends and at this time the exact location of the offcuts from the tubes was not established.

The only other general microstructural observation of note is that based on selected area diffraction patterns it was found that the α-Zr grains are elongated in the [001] direction.

(ii) Intermetallic Precipitates

Intermetallic precipitates, other than the β-phase, were only found in tubes Q19 and K23. These precipitates are very difficult to distinguish within the high dislocation density α-grains. The precipitates were somewhat easier to see in the annealed specimens and probably future studies should use only annealed specimens. However by annealing one runs the risk of eliminating or changing some other microstructural feature that is influencing the corrosion/hydriding behaviour.

The precipitates were identified by selected area diffraction as the intermetallic phase Zr_2Fe. Zr_2Fe has a tetragonal structure with a = 0.646 nm and c = 0.554 nm. Most of these Zr_2Fe precipitates had a poly-

gonal shape and an example from Tube Q19 is given in Figure 3 which includes the bright field image, the dark field image and the diffraction pattern. The diffraction pattern is for a [124] orientation of Zr_2Fe and [131] orientation of the α-Zr. In tube K23 a second type of Zr_2Fe precipitate was found which had a round shape, Figure 4. There were much fewer round precipitates than polygonal-shaped precipitates. Sizes of the Zr_2Fe precipitates ranged from 40-140 nm. Based on the TEM micrographs, an estimate was made of the amount of these Zr_2Fe precipitates and was found to be less than 0.1% on an area basis. Table 3 summarizes the data on precipitates identified, their size, shape and number of particles seen in one thin foil.

DISCUSSION

There appear to be very few of these intermetallic particles present in the Zr-2.5wt%Nb and we have only had success in identifying them in tubes Q19 and K23. It is possible that annealing of some of the other tubes would allow us to find these precipitates in those tubes, but obviously there would be a very low volume fraction present. All these intermetallic precipitates were identified as Zr_2Fe and they had either a polygonal or round shape.

The intermetallic precipitates are different from those found in the Zircaloys which are the Laves phase type compounds $Zr(CrFe)_2$. Thus the intermetallic precipitates in the Zircaloys are richer in Fe (or Cr) than those in Zr-2.5wt%Nb. This is not surprising given the higher Fe and Cr in Zircaloy than in Zr-2.5wt%Nb.

It may, or may not, be significant that Zr_2Fe has only been found in the tubes with the larger grain sizes. Examination of a further set of tubes would be required to establish only definite trends.

FUTURE WORK

There are two areas that appear to warrant further work, namely:

(i) Examination of other tube samples for presence of Zr_2Fe (or other) precipitates.

(ii) Quantitative determination of the α-grain sizes. Before this is done, the location of the offcut within the pressure tube should first be established. We would wish to compare grain sizes at the same location along the length.

Table 1

Samples Examined and Number of Thin Foils Produced

Tube Identification Number	Number of Thin Foils Prepared	Number of 'Good' Thin Foils For Examination
B11	7	4
K23	5	4
M4	5	3
N11	6	3
P5	5	2
B10	5	2
Q19	5	4
R22	8	5
S15	6	4
K23 (Annealed)	10	>4*
Q19 (Annealed)	10	>4*

* not all thin foils examined at this stage.

Table 2

Grain Sizes of Tubes as Measured by SEM and TEM Techniques, Listed in Order of Decreasing Grain Size

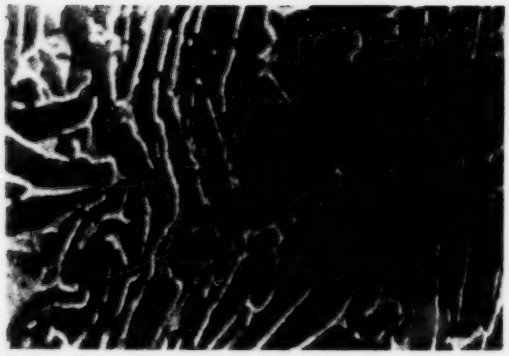
Tube Identification Number	Grain Size* of α-Zr Grains
Q19	Large
B11	Large
K23	Large
R22	Large
N11	Medium
S15	Medium
M4	Small
P5	Small
P10	Small

*Grain size is relative and quoted in qualitative terms.

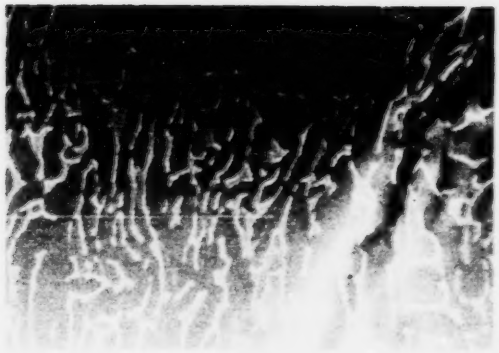
Table 3

Intermetallic Precipitates Identified in Thin Foils

Tube Identification Number	Type of Precipitate	Size nm	Shape	Number of Particles Seen in One Thin Foil
Q19	Zr_2Fe	80-140	Polygonal	~10
K23	Zr_2Fe	80	Round	1
		50-100	Polygonal	~4
Q19 Annealed	Zr_2Fe	90-140	Polygonal	~12
K23 Annealed	Zr_2Fe	40-120	Polygonal	~8
		90	Round	1



(a)



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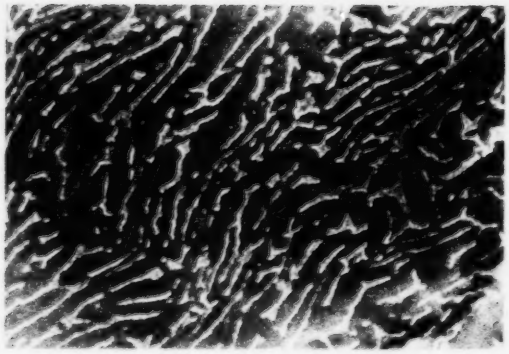
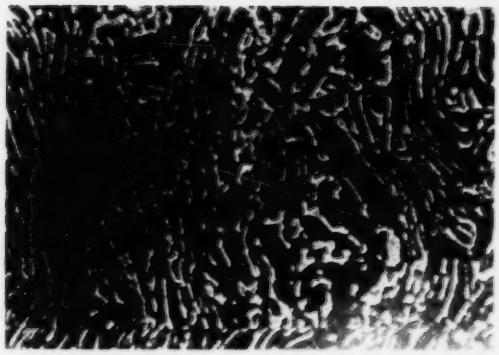


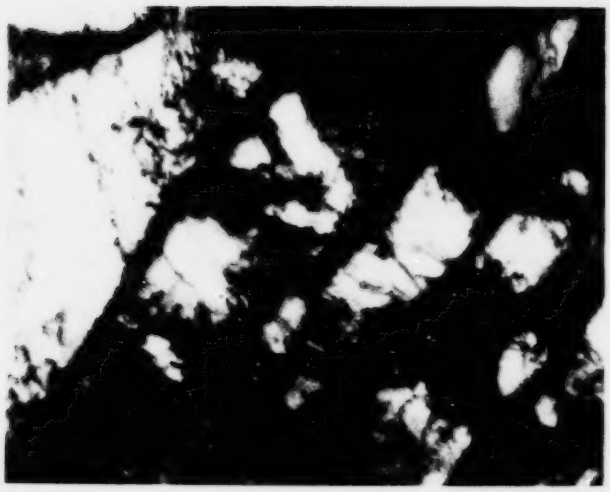
(c)



(d)

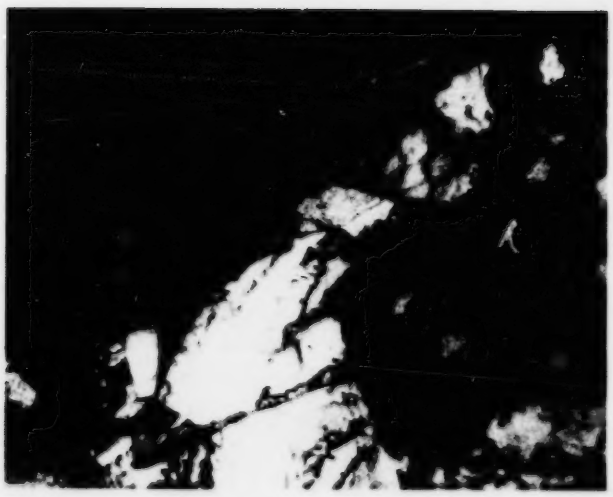
Figure 1 SEM Micrographs of Tubes (a) Q19; (b) B11; (c) K23; (d) R22. All micrographs 4000x magnification.

Figure 2 TEM Micrographs of Tubes (a) Q19; (b) B11; (c) K23; (d) R22; (e) N11; (f) S15; (g) M4; (h) P5; (i) P10. All micrographs 45,000x magnification.



(a) Q19

(b) B11



(c) K23

Figure 2 (cont'd.)

(d) R22

(e) N11

(f) S15

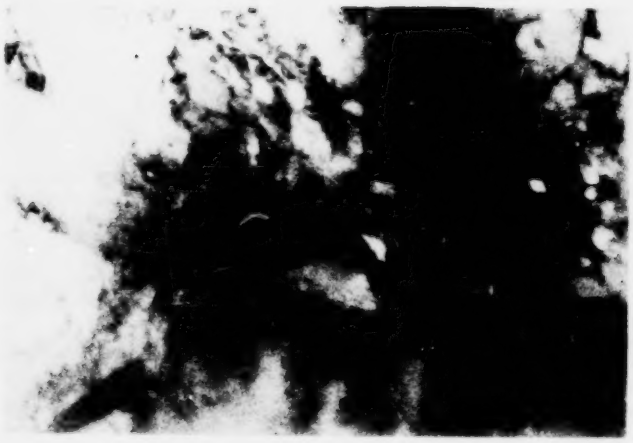
Figure 2 (cont'd.)

(g) M4

(h) P5

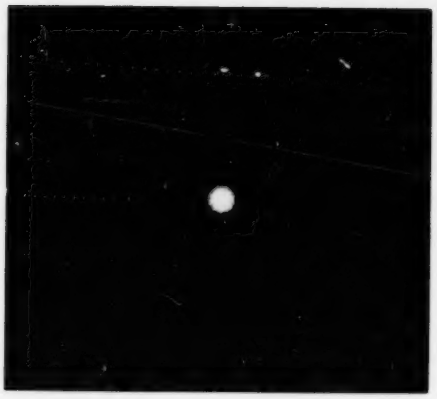
(i) P10

Figure 3 Polygonal Zr_2Fe precipitate in tube Q19. (a) Bright field micrograph, 50,000x magnification; (b) Dark field micrograph, 50,000x magnification; [N.B. The Zr_2Fe precipitate is indicated by an arrow in (a) and (b)]. (c) Selected Area Diffraction pattern from precipitate and matrix; (d) Indexing of Selected Area Diffraction pattern.

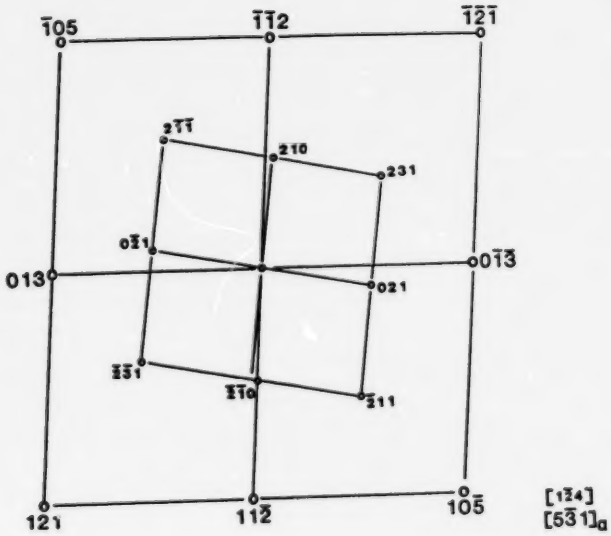


(a)

(b)



(c)



(d)

Figure 4 Bright field TEM micrograph of round Zr_2Fe precipitate (arrowed) in tube K23. Magnification 50,000x.

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